ELECTROLYTIC CONDUCTANCE OF LITHIUM BROMIDE IN ACETONE AND ACETONE-BROMOSUCCINIC ACID SOLUTION

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PREFACE

This dissertation is concerned with the investigation of the electrolytic conductance of lithium bromide in acetone and in mixtures of bromosuccinic acid and acetone. It is customary for the first chapter of a dissertation to include a statement of the problem. Due to the nature of this study such a statement has been postponed until the second chapter. The first chapter is a historical development of the Fuoss-Onsager-Skinner equation inasmuch as the problem is more meaningful when it can be related to the theory.

I undertook this investigation for several reasons. In talking with Dr. Clarence M. Cunningham, who later became my adviser, about the feasibility of the problem it became quite evident--and even more so once the research was underway--that I would have an opportunity to apply the quantitative techniques I had previously developed while working with nonaqueous solvents. In addition, it was apparent the problem necessitated my learning computer programming; I had no prior background in this field and felt a need for it in my professional career. Finally, it was my hope that I might contribute to the understanding of electrolytic conductance in solutions of low dielectric constant.

Various data had been acquired for the system by Cunningham and coworkers. The experimental work for this dissertation consisted of obtaining conductance data in acetone that was as nearly dry as possible; this appears to be an easy task, but it is not. Acetone's affinity for

water and volatility at room temperature both contribute to the difficulties. The theoretical work consisted of utilizing the Fuoss-Onsager-Skinner equation to treat all of the accumulated data.

Although an effort is presently being made to employ the International System of Units, I thought this investigation could be more readily compared to previous work by using the "electrostatic CGS" unit-system along with certain other units--such as the angstrom, Å--which are not SI units. These units are given in Appendix A and defined in terms of SI units; included in Appendix A is a list of numerical values of selected physical constants and formula masses. It should also be mentioned that common names for some compounds are used throughout the dissertation; in particular, *d*,*l*-2-bromo-butanedioic acid is referred to simply as bromosuccinic acid.

I am indebted to many individuals and several institutions. Among the individuals are Dr. Cunningham and the other members of my graduate committee--Drs. R. D. Freeman, T. E. Moore and J. B. West--and Dr. O. C. Dermer; I am particularly grateful to Dr. Cunningham for his advice and assistance with the mathematical analysis. I thank Dr. E. J. Eisenbraun for supplying the EXR-101 and apparatus for synthesizing the diazomethane and Mr. Rex Morris and Dr. J. W. Burnham for their assistance and advice concerning the bromosuccinic acid and dimethyl bromosuccinate. My gratitude is also extended to Dr. T. G. Vernardakis for helping in those situations in which two hands were insufficient, translating German for me, and caring for the conductance apparatus and dry box in my absence, to Mr. Wayne Adkins for his coffee, and to Mr. Floyd Abbott for helping me put it together. I especially give an affectionate thanks to Ms. Christine Riley for her suggestions and assistance in preparing the

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LIST OF SYMBOLS: GENERAL

A	Coefficient in conductance equation (Equation (1-113))
A	Cross-sectional area
A'	Coefficient in Debye-Hückel equation (Equation (1-24))
A''	Coefficient in Debye-Hückel conductance equation (Equation (1-32))
a	Distance of closest approach
a	Mean ionic diameter
a	Sum of ionic radii
a_o	Activity
a_+	Activity of cation
a_-	Activity of anion
$a_\pm$	Mean ionic activity
B	Coefficient in Debye-Hückel equation (Equation (1-24))
b	Characteristic parameter, Bjerrum's theory of ionic pair formation (Equation (1-66))
C	Speed of light
c	Molar concentration
c_i	Half the sum of c_+ and c_-
c_m	Molal concentration
c_n	Normal concentration
c_u	Molar concentration of undissociated salt
c_+	Molar concentration of cation

c_-	Molar concentration of anion
D	Dielectric constant
d	Distance between ions
E	Coefficient in conductance equation (Equation (1-88))
E'	Coefficient in conductance equation (Equation (1-99))
E_1'	Term in coefficient of conductance equation (Equation (1-100))
E_2'	Term in coefficient of conductance equation (Equation (1-100))
$E_n(x)$	Integral exponential function (Equation (1-70))
$E_p(b)$	Integral exponential function (Equation (1-107))
e	Base for natural logarithms
F	Force
F(z)	Continued fraction (Equation (1-80))
$\mathcal{F}$	Faraday constant
f	Activity coefficient
f	Rational activity coefficient
f_u	Activity coefficient of undissociated salt
f_+	Activity coefficient of cation
f_-	Activity coefficient of anion
$f_\pm$	Mean ionic activity coefficient
f(b)	Function given by Equation (1-111)
G	Coefficient in conductance equation (Equation (1-84))
$\overline{G}$	Chemical potential
$\overline{G}^\circ$	Chemical potential for standard state
G(b)	Function given by Equation (1-106)
g	Conductance coefficient
H	Coefficient in conductance equation (Equation (1-84))

$H(b)$	Function given by Equation (1-104)
$h(b)$	Function given by Equation (1-124)
I	Electric current
J	Cell constant
J'	Uncorrected cell constant
$J(a)$	Coefficient in conductance equation (Equation (1-88))
j	Electric current density
K_o	Proportionality constant for formation constant (Equation (1-97))
K_A	Association equilibrium constant
K_D	Dissociation equilibrium constant
$K(b)$	Function given by Equation (1-102)
$K'(b)$	Function given by Equation (1-118)
k	Boltzmann constant
L	Coefficient in conductance equation (Equation (1-113))
L_1	Term in coefficient of conductance equation (Equation (1-121))
L_s	Specific conductance
$L_2(b)$	Function given by Equation (1-123)
ℓ	Distance between electrodes
M_1	Parameter in Jones-Dole equation (Equation (5-2))
M_2	Parameter in Jones-Dole equation (Equation (5-2))
M_3	Slope of Falkenhagen limiting law (Equation (5-4))
N	Avogadro's number
$N'(b)$	Function given by Equation (1-109)
$N''(b)$	Function given by Equation (1-112)
n	Number of ions per unit volume

P	Empirical constant in extended Debye-Hückel equation (Equation (1-31))
Q	Function defined by Equation (1-35)
$Q(b)$	Integral defined by Equation (1-65)
q	Electric charge
q'	Bjerrum distance (Equation (1-68))
R	Electrical resistance
R_a	Known electrical resistance
R_b	Known electrical resistance
R_r	Adjustable electrical resistance
R_s	Electrical resistance of shunt
R_x	Unknown electrical resistance
R	Ideal gas constant
r	Radius
r	Distance
S	Onsager tangent (Equation (1-46))
S'	Empirical constant in conductance equation (Equation (1-161))
T	Kelvin temperature
T_1	Function given by Equation (1-110)
t	Celsius temperature
t_o^+	Transference number of cation at infinite dilution
t_o^-	Transference number of anion at infinite dilution
V	Electric potential difference
v	Velocity
X	Electric field strength
ΔX	Electric field strength caused by relaxation effects

Y	Function defined by Equation (1-67)
Z	Number of charges on an ion
Z_+	Number of electronic charges on cation
Z_-	Negative of number of electronic charges on anion
z	Variable defined by Equation (1-79)
α	Term for relaxation effect in Onsager tangent (Equation (1-46))
β	Bjerrum distance multiplied by two (Equation (1-108))
β_e	Term for electrophoretic effect in Onsager tangent (Equation (1-46))
Γ	Euler's constant
γ	Degree of dissociation
γ	Fraction of electrolyte existing as free ions
δ	Density of solution
δ_s	Density of acetone
ε	Electric charge of proton
ζ	Boltzmann exponent
η	Viscosity of solvent
η'	Viscosity of solution
η_{rel}	Relative viscosity (Equation (5-3))
θ	Phase angle
κ	Reciprocal of radius of ion atmosphere (Equation (1-22))
Λ	Equivalent conductance (Equation (1-2))
$\delta\Lambda$	Calculated equivalent conductance minus experimental equivalent conductance
Λ_o	Equivalent conductance at infinite dilution
Λ_o'	Function given by Equation (1-86)
Λ_d	Equivalent conductance from Equation (1-49) with c_i substituted for c_n

Λ_i	Equivalent conductance due to free ions
λ^+	Equivalent conductance of cation
λ^-	Equivalent conductance of anion
λ_o^+	Equivalent conductance of cation at infinite dilution
λ_o^-	Equivalent conductance of anion at infinite dilution
λ^i	Equivalent conductance of ith ion
λ_o^i	Equivalent conductance of ith ion at infinite dilution
μ	Ionic strength (Equation (1-23))
ν	Total number of ions produced by dissociation of one formula unit of electrolyte
ν_+	Number of cations produced by dissociation of one formula unit of electrolyte
ν_-	Number of anions produced by dissociation of one formula unit of electrolyte
π	Pi
ρ	Specific resistance (Equation (1-3))
τ	Ratio of Bjerrum distance to Debye-Hückel distance (Equation (1-101))
ψ	Electrical potential

LIST OF SYMBOLS: STATISTICAL

F_i	Condition equations for least squares method (Equation (6-6))
$F_{(c\gamma)_i}$	Partial derivatives of F_i with respect to $(c\gamma)_i$
$F_{(K_A)_i}$	Partial derivatives of F_i with respect to $(K_A)_i$
F_{L_i}	Partial derivatives of F_i with respect to L_i
F_{Λ_i}	Partial derivatives of F_i with respect to Λ_i
$F_{(\Lambda_\circ)_i}$	Partial derivatives of F_i with respect to $(\Lambda_\circ)_i$
h_{ij}	Elements of inverse matrix
L_i	Function defined by Equation (6-13)
W_i	Weight of an observation
$\sigma_{c\gamma}$	Standard deviation of the product, $c\gamma$
σ_{K_A}	Standard deviation of K_A
σ_L	Standard deviation of L
σ_Λ	Standard deviation of Λ
$\sigma_{\Lambda_\circ}$	Standard deviation of $\Lambda_\circ$
$\sigma_\circ^2$	Variance of unit weight
σ_i^2	Variance
σ_{ext}^2	External estimate of variance

CHAPTER I

EVOLUTION OF THE FUOSS-ONSAGER-SKINNER EQUATION

This chapter is divided into three sections which are arranged in chronological order. Each succeeding section covers a shorter time period and embraces a smaller breadth of electrolytic solution theory. This approach is being utilized because of the vast amount of work which has been done in electrolytic solution theory--much of which is beyond the scope of this dissertation. The first section includes electrolytic solution theory in general; the second section consists of that portion of electrolytic solution theory relating to conductance; the third section is restricted to electrolytic conductance theory for systems in which the frequencies, applied voltages and dielectric constants are low.

The Theory of Electrolytic Solutions Prior to the Twentieth Century

Toward the end of the eighteenth century Galvani (1) inadvertently discovered the effect of an electric charge on the nerve and muscle of a frog's leg. Shortly thereafter Volta (2) discovered the voltaic pile, which, for the first time, made it possible to produce an electric current of great enough magnitude to cause measurable electrochemical effects. Volta divided conductors into two classes which

correspond to what are presently designated as metallic and electrolytic conductors.[1] Almost immediately the voltaic pile was used to generate chemical reactions.

About 1805 Grotthuss proposed a theory of electrolytic conductance which was accepted for several decades. Grotthuss postulated the existence of charged atoms during and only during the passage of an electric current through the conducting solution. He believed that the positive and negative poles of an electrolytic cell exert forces similar to magnetic forces which are inversely proportional to the square root of the distance; these forces were supposed to act in opposite directions on the two components of the electrolytic solution, one component being attracted and the other repelled. Grotthuss postulated further that even during the passage of the current the ions are not independent of one another, but rather the charge is passed from atom to atom by means of a chain mechanism (3).

The first quantitative treatment in electrochemistry was performed by Faraday (4) in 1833 and his conclusions are summarized in Faraday's laws. Faraday accepted the Grotthuss theory in general. He showed, however, that the electrical force is not centered at the poles of the electrolytic cell, but extends throughout the solution, and thus proved the inverse square relation of Grotthuss to be unsound (5). Both Faraday and Daniell assumed that electrolysis consists of the passage of electricity by ions which are discharged at

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[1] In electrolytic conductors the electrical energy is carried by charged particles of atomic or molecular dimensions and flows with a transport of matter; in metallic conductors current flow involves electrons only and there is no transport of matter.

the electrodes (3). In 1839 Daniell (6) proposed ionic structures which are similar to those presently in use. Many erroneous notions were published by electrochemists during this period. In an effort to systematize the terminology for electrochemistry, Faraday consulted with Whewell who recommended many of the names still in use today (3) (7) (8).

Grotthuss' theory was attacked by Clausius, who argued that if ions depend on the application of an electric current for their existence then electrolytic solutions would not obey Ohm's law, but repeated experiments had shown that Ohm's law was obeyed. Hittorf performed some quantitative experiments which showed that ions move with different speeds; in addition he stated that ions must exist separately for most of the time during the passage of an electric current. These ideas were in contrast to Grotthuss' conclusion that ions existed only momentarily and that all ions migrated at the same speed. Kohlrausch developed a method for measuring electrolytic conductances using alternating current and obtained very precise data (3).

In 1887 Arrhenius (9) published his famous dissociation theory in which it was postulated that electrolytes in aqueous solutions are dissociated into free ions regardless of whether or not an electric current is passing through the solution. He assumed that electrolytes are partially dissociated into ions and that the degree of dissociation, γ, depends upon the concentration--increasing with dilution. His dissociation hypothesis furnished plausible interpretations for the conductance data which had been obtained by Hittorf and Kohlrausch (10). In addition it led to an explanation of the observations by Raoult and

van't Hoff (11) of anomalies in colligative properties of electrolytic solutions (12).

Ostwald (13) assumed that the degree of dissociation is given by

$$\gamma = \frac{\Lambda}{\Lambda_\infty}, \tag{1-1}$$

where Λ and Λ_∞ are the equivalent conductances of the solution at the specified concentration and at infinite dilution, respectively, and Λ is defined by the expression

$$\Lambda = 1000 \frac{L_s}{c_n}, \tag{1-2}$$

in which c_n is the concentration expressed in equivalents per liter and L_s is the specific conductance. The specific conductance is the reciprocal of the specific resistance, ρ, which is defined by

$$\rho = \frac{X}{j}, \tag{1-3}$$

where X is the electric field strength and j is the current density. The current density is the total charge carried across one cm^2 in one s and is given by the sum of the products of the number of ions per unit volume, n, and their charge, q, and the velocity, v, with which they move; that is,

$$j = \sum_i n_i q_i v_i, \tag{1-4}$$

where i, the summation index, refers to the ionic species in the solution. For the case of two parallel electrodes which have the same shaped cross-sectional area and are placed so that any line drawn perpendicularly from the face of one electrode will intersect the face of the other electrode,

$$X = \frac{V}{\ell} \tag{1-5}$$

and

$$j = \frac{I}{A}, \tag{1-6}$$

where V is the electric potential difference between the electrodes, ℓ the distance between the electrodes, I the current and A the cross-sectional area of the electrode. Therefore,

$$\rho = \frac{X}{j} = \frac{V/\ell}{I/A} = \left(\frac{V}{I}\right)\left(\frac{A}{\ell}\right). \tag{1-7}$$

Since V/I is the resistance, R,

$$\rho = R\left(\frac{A}{\ell}\right) \tag{1-8}$$

and

$$L_s = \frac{1}{\rho} = \frac{1}{R}\left(\frac{\ell}{A}\right). \tag{1-9}$$

The specific resistance represents the resistance of a one-cm cube of the conductor; the numerical value of the specific conductance is equal to the length in cm of a one-Ω conductor which has a one-cm^2 cross-section.

If the law of mass action of Guldberg and Waage is used to obtain the dissociation equilibrium constant, K_D (which is a function of temperature), the following expression can be obtained for a 1:1 electrolyte, in which c is the molar concentration:

$$K_D = \frac{c\gamma^2}{1-\gamma}. \tag{1-10}$$

Ostwald combined Equations (1-1) and (1-10) and obtained what is referred to as Ostwald's dilution law which may be written as

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_\circ} + \frac{c\Lambda}{K_D\Lambda_\circ^2}. \tag{1-11}$$

A plot of $1/\Lambda$ versus $c\Lambda$ should yield a straight line with a slope of $1/K_D\Lambda_\circ^2$ and an intercept at $1/\Lambda_\circ$ (14). This was found to be true for

many electrolytic solutions--the "weak" electrolytes, which are poor electrical conductors, conform to the law and the "strong" electrolytes, which are good electrical conductors, do not. Arrhenius' hypothesis attributes all of the changes of equivalent conductance with concentration to the change in γ and assumes that the mobility of the ions is independent of concentration.

The Arrhenius theory leads to the conclusion that for dilute solutions the equivalent conductance should be a linear function of the concentration. However, Kohlrausch had found experimentally that strong electrolytes give conductance curves which are not linear functions of the concentration for dilute solutions; he thought that the curves were best represented as linear functions of the square root of the concentration. Values of Λ_o for strong electrolytes can be obtained by plotting Λ versus $\sqrt{c}$, extrapolating the curve to zero concentration and noting the intercept.[2] When this method is applied to weak electrolytes, Λ_o cannot be obtained because the plots are curved and very steep at the intercept. Kohlrausch's law of the independent migration of ions may be applied to obtain values for Λ_o of weak electrolytes. This law is frequently expressed as

$$\Lambda_o = \lambda_o^+ + \lambda_o^-, \qquad (1\text{-}12)$$

where λ_o^+ and λ_o^- are the equivalent conductances of the cation and anion, respectively, at infinite dilution (3).

At the close of the nineteenth century both thermodynamic investigations and conductance measurements served to confirm the Arrhenius

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[2]The curve obtained when the equivalent conductance is plotted against the square root of the concentration is called a phoreogram (15).

theory; however, there was much conflicting experimental evidence which indicated that the theory does not give a lucid explanation of electrolytic conductance. Probably part of the controversy regarding the Arrhenius theory was the result of some misunderstandings. There is some question as to whether the opponents of the theory denied the actual existence of ions or only the assumption that oppositely charged ions were independent of each other. Classifying electrolytes as weak and strong was found to be even more unsatisfactory and bewildering as the investigation of systems involving nonaqueous solvents began.

The Development of Electrolytic Conductance Theory From 1900 to 1950[3]

In 1903 Roeber (17) read a paper at the general meeting of the American Electrochemical Society on the theoretical properties of free ions in solutions which he concluded with the following:

> The trouble seems to me to be right at the fundamental point of the model. If Arrhenius' model is to be used, the first thing necessary is to find an exact method of measuring the degree of ionization, i.e., the ratio of the ionized molecules to the total number of dissolved molecules. According to Arrhenius' model, we should have several methods of measuring the degree of ionization, but in many cases the results of the different methods don't agree together. Hence the battle royal between Arrhenius, Jahn, Nernst and Plank, on the question which method is the right one. This situation seems, in my opinion, to indicate an inherent weakness in the fundamental conception of Arrhenius' model. While we must admit this, it is only fair to say that even for more concentrated solutions Arrhenius' model represents an approximation of the truth, and has proven very useful in many respects, but for concentrated solutions Arrhenius' model cannot be considered to represent the facts to such a

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[3]A review article entitled "Fifty Years of Electrochemical Theory" which covers this period has been written by Hamer (16).

> degree of completeness and truth as is found to be the case for infinitely dilute solutions. ...Theories are tools we have, and it would be foolish to depreciate the usefulness of a tool because it is not perfect.

During the next few years many chemists began to accept the idea that electrolytes must be classed either as being completely dissociated into ions at all concentrations (strong electrolytes) or as being incompletely dissociated (weak electrolytes). This answered the question of why strong electrolytes do not obey the Ostwald dilution law, but not of why their equivalent conductances decrease with an increase in their concentration. Various explanations were offered for the observed variations in conductance. For example, Washburn (18) (19) (20) (21) published several papers on the conductance of concentrated solutions; he stated that an explanation for the variation of conductance with concentration of an aqueous salt solution should include such factors as the change in the quantity of the salt, the ionizing power of the medium, the viscosity of the medium, the degree of hydration, the possible formation of complex ions, a Grotthuss chain action and a change in the degree of ionization of the water. Walden (22) believed that at infinite dilution the motion of ions should depend only upon their nature and the solvent if separate ions move independently. He found that the product of the viscosity (the reciprocal of the fluidity), η, of the solvent and the equivalent conductance at infinite dilution is often constant, independent of the temperature; that is,

$$\Lambda_\infty \eta = \text{constant.} \qquad (1\text{-}13)$$

This is referred to as Walden's rule and is derivable from Stokes'

law.[4] Kraus and Bray (25) showed that this rule does not hold accurately. They also concluded that all solutions of binary electrolytes obey the same dilution law and that for a given electrolyte in different solvents the trend of the conductance curve is determined by the dielectric constant of the solvent. Various dilution law equations were proposed by different investigators.

Before 1920 several people attempted to explain the variations of conductance with electrolyte concentration in terms of electrostatic effects. Of these, only Milner (26) (27) had correctly visualized the problem. He assumed that a salt is completely dissociated into ions in solution and accounted for the deviations from ideal solution behavior in terms of interionic forces between the ions. Milner's treatment involved an application of the virial theorem and depended on the numerical evaluation of the sum of a series which could not be formulated in a compact mathematical equation; however, his method gave a theoretical basis for the establishment of the fact that electrolytic solution properties are the consequence of Coulomb forces between the ions.

During this period exact methods for treating the thermodynamics of solutions were developed. The work of Lewis (28) (29) proved to be

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[4]Stokes (23) derived the equation

$$F = 6\pi\eta rv, \qquad (1\text{-}14)$$

which gives the force, F, required to move a spherical body of radius r at a velocity v through a continuous medium of viscosity η. Derivations of Stokes' law and Walden's rule are given by Fuoss and Accascina (24) who state that the derivation of Walden's rule from Stokes' law " is simple mathematically, but the result is subject to a number of physical approximations which are hazardous."

most satisfactory. He proposed an activity, a_o, such that the laws of ideal solutions are obeyed if concentrations are replaced by activities. The activity of a substance may be defined by the equation

$$\overline{G} = \overline{G}^\circ + RT\log_e a_o, \qquad (1\text{-}15)$$

where $\overline{G}$ is the chemical potential, $\overline{G}^\circ$ the chemical potential for the substance in its standard state, R the ideal gas constant and T the thermodynamic temperature. The activity coefficient, f, is related to the activity by the expression

$$a_o = f \times (\text{concentration}) \qquad (1\text{-}16)$$

and has dimensions of reciprocal concentration units. The standard state is chosen so that f approaches unity as the concentration approaches zero. For a substance which is ionized into ν_+ cations and ν_- anions its mean ionic activity, $a_\pm$, is given by the expression

$$\overline{G} = \overline{G}^\circ + \nu RT\log_e a_\pm, \qquad (1\text{-}17)$$

where

$$\nu = \nu_+ + \nu_- \qquad (1\text{-}18)$$

and

$$a_\pm = (a_+^{\nu_+} a_-^{\nu_-})^{1/\nu}, \qquad (1\text{-}19)$$

in which a_+ and a_- are the individual ionic activities (nonthermodynamic quantities) for the cation and anion, respectively.

In 1923 Debye and Hückel (30) (31) presented a theory of electrolytic solutions which is approached from the point of view of thermodynamics. They simplified Milner's treatment by replacing all of the ions, except the reference ion which is at the origin, with a continuous space charge rather than trying to determine the electrostatic potential energy as a sum over all pairs of ions; this eliminated the

slow converging sums. The theory is based upon the following assumptions: (1) The ionic interaction between ions is completely determined by Coulomb forces--a given ion is surrounded by an "ionic atmosphere" in which there are on the average more ions of charge opposite to the central ion than ions of the same charge as the central ion. (2) The dielectric constant of the solution is equal to that of the solvent. (3) Ions are spherical and unpolarizable charges with spherically symmetric fields. (4) The energy of interionic attraction is small in comparison to the thermal energy. (5) Strong electrolytes are completely dissociated into ions at all concentrations.

The derivation consists of combining the Poisson equation of electrostatic theory with the Boltzmann distribution function from statistical mechanics and obtaining a differential equation--the Poisson-Boltzmann equation--for the electrical potential, ψ, as a function of the distance, r, from the center of the reference ion:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) = -\frac{4\pi}{D}\sum_i n_i q_i \exp(-q_i\psi_i/kT), \qquad (1\text{-}20)$$

in which D is the dielectric constant, k is the Boltzmann constant (equal to R/N, where N is Avogadro's number) and the summation index, i, refers to the ionic species in the solution. The fraction in the exponent, $q\psi/kT$, which is represented by the symbol ζ, is the ratio of the electrostatic potential energy of one ion in the field of another to the thermal energy. The derivation of the Debye and Hückel equation is given in a number of monographs (32) (33) (34) (35) (36) (37) (38).

In order to obtain an explicit formula for ψ Debye and Hückel performed a series expansion of the Boltzmann equation, applied Assumption (4) above ($q\psi \ll kT$) and terminated the series after the second term--the first term is zero because of electroneutrality. This

approximation gives therefore an expression for the charge density which is linear in ψ. This is consistent with the principle of the linear superposition of fields which states that the potential due to two systems of charges in specified positions is the sum of the potentials due to each system separately. According to Müller (39) and Güntelberg (40) when a single ion is being charged the Gibbs free energy is obtained by integrating ψdq from zero to q, the charge. Substitution of the Debye-Hückel expression for ψ and solving for the logarithm of the rational activity coefficient, f, gives the following equation for an ion of species i:

$$\log_e f_i = \frac{-(Z_i\varepsilon)^2\kappa}{2DkT(1+\kappa a)},^5 \qquad (1\text{-}21)$$

where ε is the charge of a proton, Z is the number of charges on the ion (Z is positive for cations and negative for anions; thus the charge on the ion, q, is given by the product $Z\varepsilon$.), a is the distance of closest approach (the sum of the radii of oppositely charged ions in contact) and κ, which has dimensions of reciprocal length (κ^{-1} is the radius of the ion atmosphere.), is given by the expression

$$\kappa = \sqrt{\frac{\pi N\varepsilon^2\mu}{125DkT}}, \qquad (1\text{-}22)$$

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[5]It should be noted that the rational activity coefficient given in Equation (1-21) is a dimensionless quantity, whereas the activity coefficient in Equation (1-16) is not. The numerical value depends on the concentration scale utilized, but Equation (1-21) is used in this work only in concentration ranges in which the numerical difference between rational and molar activity coefficients is negligible; therefore, the same symbol (f) has been used to denote both activity coefficients, and the appropriate dimensions are inferred from the context. The quantitative relationships among activity coefficients are given by Harned and Owen (33).

in which μ is the ionic strength.[6] Equation (1-21) may be written in the form

$$\log_{10} f_i = \frac{-A' Z_i^2 \sqrt{\mu}}{1+Ba\sqrt{\mu}}, \tag{1-24}$$

where

$$A' = \frac{\varepsilon^3}{2.303(DkT)^{3/2}} \sqrt{\frac{2\pi N}{1000}} \tag{1-25}$$

and

$$B = \sqrt{\frac{8\pi N \varepsilon^2}{1000DkT}}. \tag{1-26}$$

The parameters A' and B are constants (which can be evaluated) for a given solvent at a given temperature. The mean ionic activity coefficient, $f_\pm$, is defined by the equation

$$f_\pm = (f_+^{\nu+} f_-^{\nu-})^{1/\nu}, \tag{1-27}$$

where f_+ and f_- are the individual ionic activity coefficients for the cation and anion, respectively; it is given by the relation

$$\log_{10} f_\pm = \frac{Z_+ Z_- A' \sqrt{\mu}}{1+Ba\sqrt{\mu}}, \tag{1-28}$$

in which Z_+ is the number of electronic charges on the cation and Z_- is the negative of the number of charges on the anion. For very dilute solutions--as μ approaches zero--Equation (1-24) reduces to

$$\log_{10} f_i = - A' Z_i^2 \sqrt{\mu} \tag{1-29}$$

and Equation (1-28) reduces to

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[6] Lewis and Randall (41) defined ionic strength by the equation

$$\mu = \sum_i c_i Z_i^2 / 2, \tag{1-23}$$

where the summation index, i, refers to each ionic species in the solution.

$$\log_{10} f_{\pm} = A' Z_+ Z_- \sqrt{\mu}. \qquad (1\text{-}30)$$

Equations (1-29) and (1-30) are limiting forms of the Debye-Hückel equation. These limiting forms are also obtained as a approaches zero--that is, for point charges.

The Debye-Hückel theory indicates that the activity coefficient does have a physical significance and is more than just a correction factor. Equations (1-24) and (1-28) also take into account the ionic charge--the Arrhenius theory does not. The theory agrees with experimental results in only very dilute solutions. It is successful when applied to solutions in which the ratio of the electrical to the thermal energy of the ions is very small--that is, when the ions are not highly charged, when the dielectric constant of the medium is high and when the ions are large. Hückel (42) realized the theory requires the dielectric constant of the solution instead of that of the solvent. He thought that the dielectric constant decreases linearly with the solute concentration and modified Equation (1-24) to

$$\log_{10} f_i = \frac{- A' Z_i^2 \sqrt{\mu}}{1+Ba\sqrt{\mu}} - P\mu, \qquad (1\text{-}31)$$

where P is an empirical constant which is determined experimentally. The Debye-Hückel theory has been thoroughly scrutinized by many theorists, some of whom gave a more extended equation; for example, some modifications of the theory include the higher powers of ψ in the series expansion (43) (44). All conclude that their treatments for dilute solutions lead to the limiting Debye-Hückel equation. Some more recent extensions of the Debye-Hückel limiting law, with applications to both ionic solutions and plasmas, are given by Kelbg (45). Guggenheim (46) (47) has given an accurate numerical solution of the

Poisson-Boltzmann equation.

Debye and Hückel (31) also considered the more complicated problem of conductance--an irreversible process. They postulated that the decrease in equivalent conductance of strong electrolytes with increase in concentration is primarily due to a decrease in the mobilities of the ions. If a potential gradient is applied to an electrolytic solution, a given ion will tend to move with its own characteristic velocity. The ion atmosphere--which is of opposite sign--will tend to move in the opposite direction and its action appear to involve the movement of the solvent; this retarding effect is called the electrophoretic effect. Also, a given ion tends to move its ion atmosphere with it when a potential is applied to the system. A finite time is required for the ion atmosphere to adjust to its new location. The lag causes a dissymmetry in the potential field about the ion, the field being greater behind the ion than in its immediate vicinity. This effect--the relaxation-time effect--is independent of the viscosity of the medium and dependent upon the limiting conductance of the ion. Debye and Hückel neglected the thermal motion of the reference ion and in accounting for the electrophoretic effect assumed a Stokes radius for the moving ion.[4] They obtained a good first approximation and showed that at low concentration the equivalent conductance should be a linear function of the square root of concentration. Kohlrausch had deduced this, as mentioned previously, from his experimental data quite some time before (3). For a given temperature the Debye-Hückel conductance equation can be written in the form

$$\Lambda = \Lambda_o - A''\sqrt{C_n}, \qquad (1\text{-}32)$$

where A'' is a constant containing the radius of the ion, which means that A'' cannot be calculated theoretically.

In 1926 Onsager (48) (49) extended and improved the conductance theory of Debye and Hückel in such a manner that many of the difficulties and theoretical objections to the original treatment were overcome. He showed how the electrophoretic effect can be calculated without the necessity of knowing the ionic radius; he directed attention to the fact that if a constant force is applied to an ion, the ion does not move through the solution in a straight line; he allowed for the mutual effect of the relaxation of both ionic atmospheres on each other. Onsager took into account the Brownian movement of the ions and applied statistical methods to obtain his final conductance equation. The velocity of an ion as it moves through a solution under a potential gradient is given as the algebraic sum of the velocity at infinite dilution and the changes in velocity caused by the two opposing effects mentioned in the preceding paragraph.

In the case of a binary electrolyte the ionic equivalent conductance of the ion i, λ^i, is given by the equation

$$\lambda^i = \left[\lambda_o^i - \frac{|Z_i|\varepsilon F\kappa}{6\pi\eta C(10^{-8})}\left(\frac{1}{1+\kappa a}\right)\right]\left(1 + \frac{\Delta X}{X}\right), \qquad (1\text{-}33)$$

where λ_o^i is the ionic equivalent conductance at infinite dilution, F is the Faraday constant, C is the speed of light, a is the mean ionic diameter, X is the external electric field strength and ΔX is the electric field strength--which opposes the external field--caused by the relaxation effect. (The factor $C \times 10^{-8}$ converts esu into V so that F is expressed in C eq^{-1} while all other quantities are expressed in electrostatic CGS units.) For the relaxation effect on the conductance

of very dilute solutions Onsager obtained the following limiting law:

$$\frac{\Delta X}{X} = \frac{Z_+Z_-\varepsilon^2 Q\kappa}{3DkT(1+\sqrt{Q})}, \tag{1-34}$$

in which Q is defined by the expression

$$Q = \left(\frac{-Z_+Z_-}{Z_+-Z_-}\right)\left(\frac{\lambda_o^+ + \lambda_o^-}{Z_+\lambda_o^- - Z_-\lambda_o^+}\right). \tag{1-35}$$

Substitution of Equation (1-12) into Equation (1-35) yields

$$Q = \left(\frac{-Z_+Z_-}{Z_+-Z_-}\right)\left(\frac{\Lambda_o}{Z_+\lambda_o^- - Z_-\lambda_o^+}\right) = \left(\frac{-Z_+Z_-}{Z_+-Z_-}\right)\left(\frac{1}{Z_+\lambda_o^-/\Lambda_o - Z_-\lambda_o^+/\Lambda_o}\right). \tag{1-36}$$

The transference numbers of the cation, t_o^+, and the anion, t_o^-, at infinite dilution are given by

$$t_o^+ = \frac{\lambda_o^+}{\Lambda_o} \tag{1-37}$$

and

$$t_o^- = \frac{\lambda_o^-}{\Lambda_o}, \tag{1-38}$$

respectively. Therefore, Equation (1-35) may be written as

$$Q = \frac{-Z_+Z_-}{(Z_+-Z_-)(Z_+t_o^- - Z_-t_o^+)}.^{7} \tag{1-39}$$

Substitution of Equation (1-34) into Equation (1-33) yields

$$\lambda^i = \left[\lambda_o^i - \frac{|Z_i|\varepsilon F\kappa}{6\pi\eta C(10^{-8})}\left(\frac{1}{1+\kappa a}\right)\right]\left[1 + \frac{Z_+Z_-\varepsilon^2 Q\kappa}{3DkT(1+\sqrt{Q})}\right]. \tag{1-41}$$

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[7]The transference number of an ionic species is the fraction of the current transported by the particular species; it is also referred to as the transport number. Inasmuch as the total current is the sum of the current carried by each of the migrating ions, it follows that the sum of the transference numbers must be unity. Thus for a binary electrolyte

$$t_o^+ + t_o^- = 1. \tag{1-40}$$

Consequently, for a symmetrical electrolyte ($|Z_+| = |Z_-|$), $Q = 1/2$ and a knowledge of the ionic equivalent conductances or transference numbers is not required.

The equivalent conductance for an electrolyte is the sum of the equivalent conductances of the constituents; therefore,

$$\Lambda = \lambda^+ + \lambda^- = \left[\Lambda_\circ - \frac{(Z_+ - Z_-)\varepsilon F\kappa}{6\pi\eta C(10^{-8})}\left(\frac{1}{1+\kappa a}\right)\right]\left[1 + \frac{Z_+ Z_- \varepsilon^2 Q\kappa}{3DkT(1+\sqrt{Q})}\right], \quad (1\text{-}42)$$

where λ^+ and λ^- are the ionic equivalent conductances of the cation and anion, respectively. Onsager made the further approximations that in very dilute solutions κa is small in comparison to unity--so that $(1+\kappa a)\simeq 1$--and that the product of the second terms of the bracketed factors of Equations (1-41) and (1-42) may be neglected in comparison to the other terms. With these approximations, Equation (1-42) may be written as

$$\Lambda = \Lambda_\circ + \frac{Z_+ Z_- \varepsilon^2 Q\kappa}{3DkT(1+\sqrt{Q})}\Lambda_\circ - \frac{(Z_+ - Z_-)\varepsilon F\kappa}{6\pi\eta C(10^{-8})}. \quad (1\text{-}43)$$

Substitution of Equation (1-22) into Equation (1-43) gives

$$\Lambda = \Lambda_\circ + \frac{Z_+ Z_- \varepsilon^3 Q\sqrt{\pi N\Lambda_\circ}}{15\sqrt{5}(1+\sqrt{Q})(DkT)^{3/2}}\sqrt{\mu} - \frac{(Z_+ - Z_-)\varepsilon^2 F\sqrt{N}}{30\sqrt{5\pi}\eta C(10^{-8})(DkT)^{1/2}}\sqrt{\mu}. \quad (1\text{-}44)$$

The Onsager limiting law, expressed in Equations (1-43) and (1-44), may be abbreviated to the equation

$$\Lambda = \Lambda_\circ - S\sqrt{\mu}, \quad (1\text{-}45)$$

in which S is the Onsager tangent and

$$S = \alpha\Lambda_\circ + \beta_\circ, \quad (1\text{-}46)$$

where

$$\alpha = \frac{-Z_+ Z_- \varepsilon^3 Q\sqrt{\pi N}}{15\sqrt{5}(1+\sqrt{Q})(DkT)^{3/2}} \quad (1\text{-}47)$$

and

$$\beta_\circ = \frac{(Z_+ - Z_-)\varepsilon^2 F\sqrt{N}}{30\sqrt{5\pi}\eta C(10^{-8})(DkT)^{1/2}}. \quad (1\text{-}48)$$

For a 1:1 electrolyte, $|Z_+| = |Z_-| = 1$, so that $Q = 1/2$ and $\mu = c_n = c$; thus for a 1:1 electrolyte, Equations (1-45), (1-47) and (1-48) may be written as

$$\Lambda = \Lambda_o - S\sqrt{c_n} = \Lambda_o - (\alpha\Lambda_o+\beta_o)\sqrt{c_n}, \tag{1-49}$$

$$\alpha = \frac{\varepsilon^3\sqrt{\pi N}}{15\sqrt{10}(1+\sqrt{2})(DkT)^{3/2}} \tag{1-50}$$

and

$$\beta_o = \frac{\varepsilon^2 F\sqrt{N}}{15\sqrt{5\pi}\eta C(10^{-8})(DkT)^{1/2}}, \tag{1-51}$$

respectively.

In 1927 Davies (50) presented a method, which he applied to strong electrolytes, for calculating dissociation constants by taking into account activity coefficients when using the mass action law; for a 1:1 electrolyte this law may be expressed by the equation

$$K_D = \frac{(c_+f_+)(c_-f_-)}{c_uf_u} = \frac{c_i^2 f_\pm^2}{c_uf_u}, \tag{1-52}$$

where c_+ and c_- are the actual molar concentrations of the cation and anion, respectively, c_i is half the sum of c_+ and c_-, c_u is the molar concentration of the undissociated salt and f_u is the activity coefficient of the undissociated salt. The degree of dissociation is given by

$$\gamma = \frac{c_i}{c}; \tag{1-53}$$

he assumed the degree of dissociation to be given also by

$$\gamma = \frac{\Lambda}{\Lambda_d}, \tag{1-54}$$

in which Λ is the observed equivalent conductance and Λ_d is the calculated equivalent conductance given by Equation (1-49) with c_i substituted for c_n. Combining Equations (1-49), (1-53) and (1-54) gives

$$\Lambda_d = \frac{\Lambda c}{c_i} = \Lambda_o - S\sqrt{c_i}, \tag{1-55}$$

from which c_i can be calculated; then c_u is obtained by subtracting c_i from c. If f_u is taken to be unity--a reasonable approximation for uncharged species in dilute solutions--Equation (1-52) may be written as

$$\frac{c_i^2}{c_u} = \frac{K_D}{f_\pm^2} \tag{1-56}$$

or

$$\log_{10}\left(\frac{c_i^2}{c_u}\right) = \log_{10}K_D - \log_{10}f_\pm^2. \tag{1-57}$$

From Equation (1-30),

$$\log_{10}f_\pm^2 = -2A'\sqrt{c_i}. \tag{1-58}$$

Substitution of Equation (1-58) into Equation (1-57) yields

$$\log_{10}\left(\frac{c_i^2}{c_u}\right) = \log_{10}K_D + 2A'\sqrt{c_i}; \tag{1-59}$$

thus, a plot of $\log_{10}(c_i^2/c_u)$ versus $\sqrt{c_i}$ gives $\log_{10}K_D$ as the intercept, from which K_D is obtained.

The Onsager equation as written in Equations (1-43), (1-44), (1-45) and (1-49) is not a conductance curve equation; it is the equation for the tangent to the curve at infinite dilution--the Onsager limiting law.[8] It is of the same form as the Debye-Hückel conductance equation given by Equation (1-32). The two constants, α and β_o, which describe the relaxation effect and electrophoretic effect, respectively, are

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[8]An anabatic phoreogram is one which approaches the Onsager tangent from above as the concentration approaches zero and a catabatic phoreogram is one which approaches the Onsager tangent from below as the concentration approaches zero. A parabatic phoreogram lies right on the Onsager tangent for a moderate range of concentration (15).

completely determined by the valence type of the solute, the dielectric constant of the solvent, the absolute temperature, the viscosity of the solvent, the ionic equivalent conductance at infinite dilution, and universal constants. Onsager and Fuoss (51) used matrix algebra methods to obtain a general solution of the equation necessary to extend the Onsager treatment to electrolytic solutions containing more than two kinds of ions (a general equation of continuity for mixtures of electrolytes) and found that for nonbinary salts the coefficient $\underline{\alpha}$ is also a function of the limiting conductance of the separate ions. It has been confirmed experimentally to be a limiting equation for dilute aqueous solutions of 1:1 electrolytes, 1:2 electrolytes and 2:2 electrolytes (52) (53) (54) (55).

It is necessary to extend measurements to even lower concentrations in nonaqueous solvents because in general these solvents have lower dielectric constants and ionic attraction is more pronounced. It has been confirmed for a number of nonaqueous solvents with a dielectric constant greater than 30 that the equivalent conductance is a linear function of the square root of the concentration of the electrolyte; in some cases the slope is in agreement with the Onsager limiting law. A number of peculiarities occurs when the dielectric constant is less than 30; for example, some solutions have both maxima and minima in their conductance curves. The phoreograms for most nonaqueous systems are catabatic. In 1927 a general discussion on the theory of strong electrolytes was held by the Faraday Society which included papers and discussion on mobilities of ions and activity by Bjerrum, Bronsted, Chapman, Debye, Fajans, Ferguson and Vogel, Fowler, Harned, Hartley and Bell, Hartley

and Raikes, MacInnes and Cowperthwaite, Onsager, Remy, Scatchard, and Ulich (56).

Assumptions in the theory are no longer valid at higher concentrations and several empirical equations have been proposed that give very good agreement with experimental data (57). One such extension of the Onsager equation for 1:1 electrolytes was proposed by Shedlovsky (58). He rearranged Equation (1-49) as follows:

$$\Lambda_o = \frac{\Lambda+\beta_o\sqrt{c_n}}{1-\alpha\sqrt{c_n}}. \qquad (1\text{-}60)$$

To this expression he added another term:

$$\Lambda_o = \frac{\Lambda+\beta_o\sqrt{c_n}}{1-\alpha\sqrt{c_n}} - S'c_n; \qquad (1\text{-}61)$$

S' is the slope of the curve for a plot of $(\Lambda+\beta_o\sqrt{c_n})/(1-\alpha\sqrt{c_n})$ versus c_n. Equation (1-61) may be rearranged to give

$$\Lambda = \Lambda_o - S\sqrt{c_n} + S'c_n(1-\alpha\sqrt{c_n}). \qquad (1\text{-}62)$$

Because of the restricted application of the Onsager equation the question arises as to whether or not other means can be used to obtain confirmatory evidence for the interionic attraction theory. Two effects which appear to confirm the theory are the Wien effect and the Debye-Falkenhagen effect.

Wien (59) (60) showed that at high applied voltages the conductance of certain electrolytes rises more rapidly than would be expected from Ohm's law--the rise in conductance being proportional to the field strength--even when the heating effect of the current is considered. At very high field strengths the conductance rises more slowly tending toward a limit. The Wien effect is found to be greatest at high concentrations and for solutions containing highly charged ions; these are

the conditions under which the electrophoretic and time of relaxation effects are expected to be greatest. In the case of weak electrolytes it was found that the high fields caused an increased ionization, referred to as the dissociation field effect or second Wien effect, which has been discussed by Onsager (61) and others. The Wien effect may be interpreted in the following manner. The absolute mobilities of ions are of the order of magnitude of 10^{-3} cm s^{-1} in a potential gradient of one V cm^{-1}. The ionic velocity is about 10^{2} cm s^{-1} when the potential gradient is 10^{5} V cm^{-1} and under these conditions an ion traverses the width of the ionic atmosphere in about 10^{-10} s. This is approximately the time required for the formation or decay of the ion atmosphere, so that in very strong fields it is possible for ions to migrate free of an ionic atmosphere (62).

In 1928 Debye and Falkenhagen (63) (64) extended the Onsager theory to alternating current conductance and predicted from theoretical considerations that if measurements of electrolytic conductance were made using very high frequency alternating current greater conductances would be obtained than if relatively low frequencies were used. Sack (65) demonstrated this dispersion of conductivity experimentally. The increase in conductance occurring with the increase in frequency of the alternating current is called the Debye-Falkenhagen effect and may be interpreted as follows. If the conductance measurements are made using low frequency alternating current a dissymmetry in the ionic atmosphere, which corresponds to the momentary velocity of the ion, will be produced at each instant. If the field alternates at a rate which is comparable with the time required for the adjustment to

occur the dissymetry will not have sufficient time to be established and the braking effect on the motion of the ion will be decreased. Therefore, theoretically the time of relaxation effect will disappear at very high frequencies. The observed changes of conductance with frequency have been found to agree qualitatively with the theory of Debye and Falkenhagen (35).

In 1931 Onsager (66) (67) applied the principle of microscopic reversibility and obtained a general reciprocal relation which is applicable to transport processes such as the conduction of heat and electricity and diffusion.[9]

Before proceeding further it will both simplify and clarify matters to adopt two terms introduced by Fuoss (15) and discontinue the use of the terms strong electrolyte and weak electrolyte. Fuoss refers to substances such as sodium chloride which exist only as lattices of ions in the pure crystalline form as ionophores and substances such as acetic acid which in certain solvents can give conducting solutions although the pure substances are nonelectrolytic neutral molecules as ionogens. The advantage of this classification is that it is based on the chemical structure of the solute and is independent of the behavior of that particular solute in any given solvent. In general the previous discussions of the Debye-Hückel-Onsager theory have involved ionophores, whereas those discussions pertaining to substances which obey the Ostwald dilution law have involved ionogens.

Even though the Onsager equation satisfactorily accounted for the

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[9]Onsager was awarded the Nobel prize in 1969 for this. The Onsager reciprocity theorem is discussed by Yourgrau (68).

limiting behavior of solutions of ionophores in solvents of high dielectric constant, it did not account for solutions which obeyed the Ostwald dilution law or solvents such as ammonia in which the phoreograms are similar to those of ionogens in solvents of high dielectric constant.

Fuoss and Kraus (69) (70) (71) (72) undertook an extensive investigation of the properties of electrolytic solutions. They studied the conductance of tetraisoamylammonium nitrate in water, dioxane, and various dioxane-water mixtures and found that specific effects due to the solvent, except viscosity, are not large; they also showed that at sufficiently low concentrations the equivalent conductance increases with dilution, even in solvents of very low dielectric constant. They gave a method for solving the conductance equations for ionophores in various solvents, including ammonia, and were able to give a complete picture of equivalent conductance over a wide range of dielectric constant by applying and extending the concept of ion association which had been given by Bjerrum (73) (74).

In order to account for deviations from the limiting Debye-Hückel activity law Bjerrum assumed the ions are rigid unpolarizable spheres in a medium of a fixed macroscopic dielectric constant, excluded ion-solvent interactions and proposed that the ions could associate to form ion pairs. Such pairs would be stable to thermal bombardment by the surrounding solvent molecules if the Coulomb potential energy of two ions in contact is large relative to $\underline{kT}$.[10] (A solvent of sufficiently

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[10]A more detailed discussion of Bjerrum's theory of ionic association is given by Harned and Owen (33); Fuoss (75) gives a rigorous discussion of another approach to the same subject.

low dielectric constant for this to occur is called a smenogenic solvent; a solvent in which the dielectric constant is high enough to prevent ion association is referred to as a smenocolytic solvent (15).) He assumed that in the case of solutions of ionophores there is an equilibrium between free ions and ion pairs, which for 1:1 electrolytes may be expressed by the chemical equation

$$C^+ + A^- \rightleftharpoons [C^+A^-]^\circ, \tag{1-63}$$

where the term in brackets is an ion pair and A^- and C^+ are the free anion and cation, respectively. According to Bjerrum's treatment the equilibrium constant for the formation of an ion pair, K_A (the reciprocal of the dissociation constant, K_D, of the associated ion pair), is given by

$$K_A = \frac{-4\pi N}{1000}\left(\frac{Z_+Z_-\varepsilon^2}{DkT}\right)^3 Q(b). \tag{1-64}$$

$Q(b)$ is defined by the integral

$$Q(b) = \int_2^b \exp(Y)Y^{-4}dY, \tag{1-65}$$

where b is defined by

$$b = \frac{-Z_+Z_-\varepsilon^2}{aDkT} \tag{1-66}$$

and Y is defined by

$$Y = \frac{-Z_+Z_-\varepsilon^2}{dDkT}, \tag{1-67}$$

in which d is the distance between the ions and d is less than the Bjerrum distance, q', which is given by the equation

$$q' = \frac{-Z_+Z_-\varepsilon^2}{2DkT}. \tag{1-68}$$

The integral $Q(b)$ reduces to

$$Q(b) = \frac{1}{6}\left[\exp(2)+E_n(-2)-E_n(-b)-\frac{\exp(b)}{b}\left(1+\frac{1}{b}+\frac{2}{b^2}\right)\right], \tag{1-69}$$

where $E_n(x)$ is the integral exponential function,

$$E_n(x) = \int_x^\infty \exp(-u)u^{-1}du = -\Gamma - \log_e x + x - \frac{x^2}{2\cdot 2!} + \cdots. \quad (1\text{-}70)$$

Values of $Q(b)$ have been calculated by Bjerrum (73) for the range $1 \leq b \leq 15$ and by Fuoss and Kraus (71) for the range $15 \leq b \leq 80$. Bjerrum assumed that two ions at a distance of $d < q'$ are associated. For 1:1 electrolytes in water at 18 °C, q' equals 3.52 Å; therefore, 1:1 electrolytes with a less than 3.5 Å will form short-range ion pairs and with a greater than 3.5 Å will not--the Debye-Hückel theory would be valid for the latter. Bjerrum (56) pointed out:

> The distinction between free and associated ions was not a chemical one, but only a mathematical device making possible an approximate calculation of the effect of interionic forces under conditions where the approximation of Debye and Hückel could not be used.

The ion pair concept is simply a handy model for representing higher terms of electrostatic interaction.

For ionogens it is assumed that a reaction occurs first between the solute and solvent to form a molecular complex which rearranges to form an ion pair and can then dissociate to form free ions:

$$CA + \text{solvent} \rightleftharpoons CA\cdot\text{solvent}, \quad (1\text{-}71)$$

$$CA\cdot\text{solvent} \rightleftharpoons [C(\text{solvent})^+A^-]^\circ, \quad (1\text{-}72)$$

$$[C(\text{solvent})^+A^-]^\circ \rightleftharpoons C(\text{solvent})^+ + A^-. \quad (1\text{-}73)$$

It is to be noted that in the case of ionophores--Equation (1-63)--the process is one of association of ions rather than dissociation of a free molecule. Fuoss and Kraus proposed triple ion formation to account for the appearance of minima in conductance curves:

$$[C^+A^-]^\circ + C^+ \rightleftharpoons [C^+A^-C^+]^+, \quad (1\text{-}74)$$

$$[C^+A^-]^\circ + A^- \rightleftharpoons [A^-C^+A^-]^-; \quad (1\text{-}75)$$

the expressions on the right side represent ion triplets. They also proposed quadrupole formation--association of ion pairs (76). Halpern and Gross (77) (78) presented a theoretical treatment of electrolytic solutions and criticized the theoretical interpretation of ion association given by Fuoss and Kraus (70) (71) (72); this criticism was refuted by Fuoss and Kraus (79). There is considerable evidence from different kinds of experiments for the existence of ion association (80) (81) (82) (83) (84) (85). Fuoss and Accascina (24) have said of two papers of Kraus (83) (84) on the subject that they "contain so much information, based on over sixty years of research experience, that no abstract (short of outright plagiarism) of them could be adequate."

The equation obtained by Fuoss and Kraus for the conductance of 1:1 electrolytes as a function of concentration is

$$\Lambda = \gamma(\Lambda_o - S\sqrt{\gamma c_n}), \tag{1-76}$$

where γ is the fraction of electrolyte existing as free ions. Equation (1-1) gives the degree of dissociation when it is assumed that ionic mobilities are independent of concentration. Inasmuch as Equation (1-1) cannot be considered to be a true representation of the degree of dissociation of an electrolyte, Bjerrum introduced the conductance coefficient, g, which is a correction factor that accounts for the concentration dependence of ionic mobilities:

$$\gamma g = \frac{\Lambda}{\Lambda_o}. \tag{1-77}$$

The conductance coefficient is defined as the ratio of the observed equivalent conductance to the value which the equivalent conductance would have at the same ionic concentration in the absence of interionic forces. Mathematically Equation (1-76) is just the Arrhenius

equation corrected for the effects of long range interionic forces; however, physically the interpretation is obviously quite different. The expression for the equilibrium constant, K_D, for the dissociation of the ion-ion pair is given as

$$K_D = \frac{c_n \gamma^2 f_{\pm}^2}{1-\gamma}, \tag{1-78}$$

which is essentially a combination of Equations (1-10) and (1-52). Equation (1-76) is obeyed exactly up to concentrations at which specific interactions of higher order than ion pairs become appreciable; it was derived on the assumption that free ions and ion pairs are the only species present. Onsager and Fuoss (49) (51) (86) have pointed out that a more complete conductance equation should contain terms of order higher than $\sqrt{c_n}$. The solution of Equation (1-76) for γ entails a series of successive approximations. Fuoss (87) simplified the calculations by introducing a variable, z, defined as follows:

$$z = S\Lambda_o^{-3/2}\sqrt{c_n\Lambda} = S\Lambda_o^{-3/2}\sqrt{1000L_s}. \tag{1-79}$$

It can be shown that $(\Lambda_o - S\sqrt{\gamma c_n})$ is equal to the product of Λ_o and the continued fraction, $F(z)$;

$$F(z) = 1 - z\{1 - z[1 - z(1 - \ldots)^{-1/2}]^{-1/2}\}^{-1/2}. \tag{1-80}$$

Thus Equation (1-76) may be rearranged and written

$$\gamma = \frac{\Lambda}{\Lambda_o F(z)}. \tag{1-81}$$

He calculated values of $F(z)$ for values of z from $z = 0.000$ to $z = 0.209$ and they are tabulated in the paper. Substitution of Equation (1-81) into Equation (1-78) and rearrangement yields the Fuoss-Kraus equation:

$$\frac{F(z)}{\Lambda} = \frac{1}{K_D\Lambda_o^2}\left(\frac{c_n\Lambda f_{\pm}^2}{F(z)}\right) + \frac{1}{\Lambda_o}. \tag{1-82}$$

In order to obtain Λ_o and K_D from conductance data a free hand extrapolation of a phoreogram is made to get a tentative value for the limiting conductance. With this tentative value, z is calculated from Equation (1-79), $F(z)$ from either Equation (1-80) or tables, γ from Equation (1-81), and $f_\pm^2$ from the equation

$$\log_{10} f_\pm^2 = 2Z_+Z_-A'\sqrt{\gamma c_n}. \qquad (1\text{-}83)$$

(Compare Equation (1-83) with the limiting forms of the Debye-Hückel equation as given by Equations (1-30) and (1-58).) Finally $F(z)/\Lambda$ is plotted against $c_n\Lambda_\pm^2/F(z)$ and for molar concentrations less than $3.2 \times 10^{-7} \times D$ (at 25 °C) a straight line is obtained which has an intercept of Λ_o^{-1} and a slope of $(K_D\Lambda_o^2)^{-1}$; such a graph is referred to as a Fuoss plot (88).

A number of functions and methods were proposed during this period by Shedlovsky (89) and others; of these the Owen (90) method is best for higher valence types. Fuoss (91) and Kraus (92) wrote review articles on the subject in 1935 and 1938, respectively, and a comparison of extrapolation methods for conductance data was given by Fuoss and Shedlovsky (93) in 1949. Other review articles on related subjects were written during this time by Debye (94), Kirkwood (95), Onsager (96), Redlich (97), and Scatchard and Epstein (98)--articles referring in particular to the role of ionic solvation were written by Robinson and Stokes (99) (100) and Bockris (101).

An experimental problem of the theory was that a knowledge of the ionic equivalent conductance was necessary except for symmetrical binary electrolytes. Because of the lack of transference number data in nonaqueous solvents the ionic equivalent conductances were obtained

by the method of Fowler (102) which appears to be a reasonable, though essentially arbitrary, assumption. The method consists of measuring the conductance of an electrolyte consisting of two large ions of high symmetry, equal size and similar constitution; it is then assumed that the transference number of each ion is one half and the ionic equivalent conductance is therefore taken to be half of the equivalent conductance. (See Equations (1-37) and (1-38).) The ionic equivalent conductances of other ions in the solvent are calculated relative to these two ions by making use of Equation (1-12). This has been done with a number of solvents; of particular interest to this dissertation is the work of Reynolds and Kraus (103) with acetone as the solvent.

Thus, at the midpoint of the twentieth century the generally accepted theory for electrolytic conductance was based on the idea that the change in conductance with concentration was due to both the mobility and the fraction of free ions for both ionophores and ionogens. The hypothesis of ion association had displaced the Arrhenius hypothesis of dissociation for ionophores.

The Development Since 1950 of the 1965 Fuoss-Onsager-Skinner Equation

As stated at the beginning of this chapter, this section is limited to the development of the Fuoss-Onsager-Skinner conductance equation which is applicable to a system involving 1:1 electrolytes in a smenogenic solvent at a low constant applied voltage and a constant low frequency. Consequently, such phenomena as the Wien effect and the Debye-Falkenhagen effect are not involved nor discussed. Though

diffusion is involved, its effects have not been studied in this work and therefore are not included here. Review articles discussing the general work on solutions of electrolytes are available; one good source of such articles is Annual Reviews of Physical Chemistry.

It was suggested that the deviations of Equation (1-49) from experimental observations might be accounted for by terms of higher order which had been neglected. Kraus and coworkers (104) (105) introduced two of what appeared to be the more important of these terms:

$$\Lambda = \Lambda_o - S\sqrt{c_n} + Hc_n + Gc_n\log_e c_n. \qquad (1\text{-}84)$$

The coefficients H and G are constants which had not been evaluated successfully on a theoretical basis. They wrote this extended equation of Onsager so that it expressed the deviation from the simple Onsager equation as a function of concentration:

$$\Lambda_o' - \Lambda_o = Hc_n + Gc_n\log_e c_n, \qquad (1\text{-}85)$$

where

$$\Lambda_o' = \frac{\Lambda+\beta_o\sqrt{c_n}}{1-\alpha\sqrt{c_n}}. \qquad (1\text{-}86)$$

If G and H are zero, values of Λ_o' calculated from Equation (1-86) using experimental data are the same as for Λ_o. If the deviation is found to be a linear function of c_n, this corresponds to a value of zero for G and a nonzero value for H:

$$\Lambda_o' - \Lambda_o = Hc_n; \qquad (1\text{-}87)$$

H is an empirical constant equal to the slope of the curve for a plot of Λ_o' versus c_n. Equation (1-87) is of the same form as Equation (1-61) which had been found to hold for a number of salts.

In 1955 Fuoss and Onsager (106) (107) presented a preliminary statement of a theoretical conductance equation which is valid for non-

zero concentrations. They summarized the derivation as follows:

> We start with the general equation of continuity which specifies the concentration of ions of one species in the vicinity of ions of the other species in a solution of electrolyte which has reached a steady state under the influence of an external force (here, an electric field). The equation is first solved, neglecting terms of higher order, but using ions of finite size rather than point charges as the model. This first-order solution is then returned to the higher-order terms in the equation of continuity. Solution of the resulting perturbation problem gives the desired expression for the relaxation effect in the mobility to terms of order c and $c\log_e c$. On combining this result with the previous value of the electrophoresis calculated to the same order, the final conductance function is obtained.

Fuoss and Onsager (108) gave the details of their derivation in 1957 and obtained an equation,

$$\Lambda = \Lambda_o - Sc^{1/2} + Ec\log_{10}c + J(a)c, \qquad (1\text{-}88)$$

which is similar in form to Equation (1-84); however, the coefficients, E and $J(a)$, were obtained from the theoretical treatment. They were able to reproduce experimental data up to about 0.01 normal for aqueous solutions of 1:1 ionophores. Thus they showed that anabatic phoreograms can be accounted for theoretically merely by a refinement of the earlier calculation--the replacement of point charges by charged spheres in the physical model.

Also in 1957 Fuoss (109) combined the new conductance equation with the law of mass action and obtained a generalized conductance equation which includes the case of association of free ions to ion pairs. He rearranged Equation (1-78) so that it was written as

$$\gamma = 1 - K_A c\gamma^2 f_{\pm}^2. \qquad (1\text{-}89)$$

In this expression, $f_{\pm}$ is obtained from Equation (1-28) by replacing μ with the actual concentration of free ions, $c\gamma$; Equation (1-28) can

then be written as

$$\log_{10} f_{\pm} = \frac{-A'\sqrt{c\gamma}}{1+\kappa a\sqrt{\gamma}}. \qquad (1\text{-}90)$$

The denominator of Equation (1-90) results from the fact that for 1:1 electrolytes

$$\kappa = B\sqrt{c}. \qquad (1\text{-}91)$$

This can be shown by substituting Equation (1-26) into Equation (1-22) and noting that $\underline{\mu} = \underline{c}$. Fuoss assumed that the conductance due to free ions, $\underline{\Lambda_i}$, is given by a form of the equation, which is valid at low concentrations ($\underline{\kappa a} \not> 0.2$), for conductance of unassociated electrolytes.[11] He replaced $\underline{c}$ throughout by $\underline{c\gamma}$ to give the actual concentration of free ions (in equivalents per liter) and wrote

$$\Lambda = \gamma\Lambda_i, \qquad (1\text{-}92)$$

where $\underline{\Lambda}$ is the observed equivalent conductance. Substitution of Equation (1-92) into Equation (1-89) gives

$$\frac{\Lambda}{\Lambda_i} = 1 - K_A c\left(\frac{\Lambda}{\Lambda_i}\right)\gamma f_{\pm}^2 \qquad (1\text{-}93)$$

or

$$\Lambda = \Lambda_i - K_A c\Lambda\gamma f_{\pm}^2. \qquad (1\text{-}94)$$

Substitution of the conductance equation for unassociated electrolytes (Equation (1-88))--with $\underline{c\gamma}$ in place of $\underline{c}$--for $\underline{\Lambda_i}$ in Equation (1-94) yields an equation for the conductance of associated electrolytes:

$$\Lambda = \Lambda_o - Sc^{1/2}\gamma^{1/2} + Ec\gamma\log_{10}c\gamma + J(a)c\gamma - K_A c\gamma f_{\pm}^2\Lambda. \qquad (1\text{-}95)$$

Fuoss included a graphical treatment for the solution of the equations

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[11] Accascina, Kay and Kraus (110) have given an experimental demonstration of the importance of this limit.

and gave an estimate of the viscosity correction which is also required if one ionic species is bulky compared to the solvent molecules.

Fuoss (111) revised the equations and rearranged the algebraic form so as to be more convenient for practical computation. Fuoss and Kraus (112) applied the method successfully to several salts in dioxane-water mixtures and showed that $\underline{K_A}$ can be represented by the expression

$$K_A \propto \exp(b). \tag{1-96}$$

Fuoss (113), using a model in which the solvent is a continuum, applied a method devised by Boltzmann (114) to the equilibrium between ion pairs and free ions which led directly to Equation (1-89), in which the value of $\underline{K_A}$ is given by

$$K_A = K_\circ \exp(b), \tag{1-97}$$

where

$$K_\circ = \frac{4\pi N a^3}{3000}. \tag{1-98}$$

Expression (1-96) is consistent with the results of Denison and Ramsey (115), who used a Born cycle to show that $\underline{K_A}$ should be a continuous function of $\underline{DT}$, and Gilkerson (116), whose model includes the effect of interaction between solvent and solute and the free volume of the solute. (Fuoss and Accascina (117) used Equation (1-97) to explain the fact that tetraethylammonium picrate is more associated in 1-butanol-methanol mixtures than is tetramethylammonium picrate.) Fuoss and co-workers (118) gave a physical description of their model as it stood in 1958 and stated it is "only a first approximation, but, until its limitations have been established, it seems pointless to consider more complicated models."

In 1959 Fuoss (119) collected the derivation and its revisions--References (106), (107), (108), (109), (111), (112), (113), (120), and (121)--in one paper in which he included a nonmathematical summary of the derivation and described methods of applying the equation to experimental data. Fuoss and Accascina (24) gave a detailed outline of the complete theory. Sadek and Fuoss (122) discussed the relative values of the terms as a function of concentration over a wide range of dielectric constants. Kay (123) gave a method of solving the equations with a high speed computer. Lind, Zwolenik and Fuoss (124) used experimental data for aqueous potassium chloride solutions to show that one form of the equation can be used to calibrate conductance cells with an accuracy of 0.01 percent up to concentrations of 0.01 N KCl. Fuoss (125) showed another method for obtaining an ion size parameter from the dependence of the Walden (22) product, $\underline{\Lambda_o \eta}$, on the dielectric constant. Petrucci (126) found that Walden's rule agrees well for some nonaqueous systems. Stern and Amis (127) wrote a review on ionic sizes and Young and Irish (128) have discussed the meaning of degree of association as determined by different methods. Wirth (129) suggested another function for estimating dissociation of electrolytes which was simpler than that of Fuoss (87) or Shedlovsky (89). Davies (130) published a monograph on ion association in 1962.

In 1962 Fuoss and Onsager began a revision of their treatment of the conductance of symmetrical electrolytes. They undertook the investigation for two reasons. First, they were dissatisfied with the arbitrary insertion of the mass action hypothesis into the argument; if ion association occurs only as a result of Coulomb forces then one

should be able to predict the decrease in electrical conductance with increasing concentration directly from the equation of continuity, the equations of motion and the Poisson equations. Second, it had been found that "$\underline{a}$ values" calculated from the linear coefficients of the equation increased systematically for a given electrolyte as the dielectric constant of the solvent mixture decreased. The dependence is either the result of mathematical approximations made in the derivation of the equation from the fundamental differential equations or the consequence of an inadequate model for the real systems. The derivation of Equation (1-88) contains two mathematical approximations--all terms which would ultimately lead to terms of order $\underline{c}^{3/2}$ or greater were deleted and in the equation of continuity the Boltzmann factor, $e^{\underline{\xi}}$, was approximated by the first three terms of its power series $(1+\underline{\xi}+\underline{\xi}^2/2)$. The effect of the first approximation can be eliminated by limiting application of Equation (1-88) to sufficiently low concentrations--that is, to concentrations in which the deviations between observed and calculated conductances are random and their root-mean-square value is within the estimated experimental error. The effect of the latter, however, is built into the final outcome at the beginning of the computation and can never be removed. Fuoss and Onsager concluded that a more realistic model is required--in particular, one which includes short range ion-solvent interactions. In the first paper of a series they considered the potential of total force, in the second paper the relaxation field, in the third electrophoresis and in the fourth the hydrodynamic and osmotic terms in the relaxation field (131) (132) (133) (134). (The abstracts from the original papers are given in Appendix B.) Fuoss (135) has discussed these factors further.

Fuoss, Onsager and Skinner (136) combined the results of the four papers in 1965 and obtained the following equation (in which the Boltzmann factor has been retained explicitly) directly from the equation of continuity, the equations of motion and Poisson's equations:

$$\Lambda = \Lambda_o - Sc^{1/2} + E'c\log_e\tau^2 - 6E'K(b)c\exp(-2\tau) + [E_1'\Lambda_oH(b) - E_2'G(b)]c - [(2b-3)/b^2]\Lambda_o\tau^3, \quad (1\text{-}99)$$

where S and b are given by Equations (1-46) and (1-66), respectively,

$$E' = E\log_{10}e = E_1'\Lambda_o - E_2', \quad (1\text{-}100)$$

$$\tau = (6E_1'c)^{1/2}, \quad (1\text{-}101)$$

$$K(b) = \frac{1}{3}\left[E_p(b) - \frac{\exp(b)(1+1/b)}{b}\right], \quad (1\text{-}102)$$

$$E_1' = \frac{\beta^2\kappa^2}{24c}, \quad (1\text{-}103)$$

$$H(b) = 2N'(b) + (1-T_1)^{-1}, \quad (1\text{-}104)$$

$$E_2' = \frac{\beta\kappa\beta_o}{16c^{1/2}} \quad (1\text{-}105)$$

and

$$G(b) = 1.9055 + 2/3b^2 - 4f(b); \quad (1\text{-}106)$$

E is given in Equation (1-88),

$$E_p(b) = \int_{-\infty}^{b}\exp(u)u^{-1}du = \frac{\exp(b)}{b}\left(1+\frac{1!}{b}+\frac{2!}{b^2}+\ldots\right), \quad (1\text{-}107)$$

$$\beta = 2q' = ab, \quad (1\text{-}108)$$

$$N'(b) = \frac{1.4681-1.2916T_1}{1-T_1} - \left[2+Q+\frac{T_1}{2(1-T_1)}\right]\kappa a, \quad (1\text{-}109)$$

$$T_1 = \exp(-b)(1+b+b^2/2), \quad (1\text{-}110)$$

$$f(b) = -\tau/3(1+Q) + (\tau^2/3)\log_e\tau - \tau^2\exp(-2\tau)K(b) + N''(b)(\tau^2/3) \quad (1\text{-}111)$$

and κ and β_o are given by Equations (1-22) and (1-51), respectively;

$$N''(b) = 2\Gamma - 1 + \log_e 2 + \log_e(2+Q) + (1-T_1)^{-1}[T_1(Q-1/2) - Q/(2+Q) + (T_1/2)\log_e(2+Q)/(1+Q)] \quad (1\text{-}112)$$

and q' and Q are given by Equations (1-68) and (1-39), respectively.[12] They simplified Equation (1-99) by dropping the τ^3 term (which is of order $c^{3/2}$) and changing the notation to a more convenient form which includes some computational approximations:

$$\Lambda = \Lambda_o - Sc^{1/2} + E'c\log_e\tau^2 + Lc - A\Lambda_o cf_{\pm}^2, \tag{1-113}$$

in which

$$L = E_1'\Lambda_o H(b) - E_2'G(b), \tag{1-114}$$

$$A = \frac{6E'K(b)}{\Lambda_o} \tag{1-115}$$

and

$$f_{\pm} = \exp(-\tau). \tag{1-116}$$

Equation (1-113) reduces to Equation (1-88) for solutions of low concentrations in smenocolytic solvents with

$$J(a) = E'\log_e(6E_1') + L - A\Lambda_o. \tag{1-117}$$

The first term, $K'(b)$, of the asymptotic expansion of $K(b)$ is

$$K'(b) = \frac{2\exp(b)}{3b^3} \tag{1-118}$$

and appears in the direct theoretical derivation of the association constant; $K(b)$ is negative for $b < 2.35$ and $K'(b)$ has a minimum at $b = 3$. Neglecting the term E_2' (which is relatively small compared to E_1') in Equation (1-100) reduces E' to $E_1'\Lambda_o$, which when substituted in Equation (1-115) along with $K'(b)$ for $K(b)$ yields

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[12]The dimensionless variable, τ, is the ratio of the Bjerrum distance (q'), where ion pair probability functions usually have their minima, to the Debye-Hückel distance (κ^{-1}), where the maximum charge of the ion atmosphere is located. It is a rational reduced variable for the description of electrolytic solutions; two electrolytic solutions which have the same value of τ are in corresponding electrostatic states, regardless of concentration, dielectric constant and temperature (137).

$$A = \frac{4\pi N a^3 \exp(b)}{3000}; \tag{1-119}$$

this is identical to the expression for K_A given by Equations (1-97) and (1-98). Consequently, Equation (1-113) gives the limiting form of Equation (1-95) as γ approaches unity if $J(a)$ is given by Equation (1-117) and A is identified with K_A. Of course, $K(b)$ cannot be interpreted as a factor in an association constant when it is negative--that is when b is less than 2.35. Equation (1-113) fits data over a somewhat wider range toward lower dielectric constants than does Equation (1-88); however, it also starts to show systematic deviations below a dielectric constant of about 25. They proposed a stochastic extension of Equation (1-99) to lower dielectric constants--where $K(b)$ is greater than unity--and formulated a general conductance equation:

$$\Lambda = \Lambda_o - Sc^{1/2}\gamma^{1/2} + E'c\gamma\log_e(\tau^2\gamma) + Lc\gamma - K_A c\gamma f_{\pm}^2\Lambda, \tag{1-120}$$

in which L is given by

$$L = L_1 + L_2(b) \tag{1-121}$$

and S, E', τ, K_A and $f_{\pm}$ are given by Equations (1-46), (1-100), (1-101), (1-97) and (1-116), respectively;

$$L_1 = 3.202E_1'\Lambda_o - 3.420E_2' + \alpha\beta_o \tag{1-122}$$

and

$$L_2(b) = 2E_1'\Lambda_o h(b) + \frac{44E_2'}{3b} - 2E'\log_e b; \tag{1-123}$$

$$h(b) = \frac{2b^2+2b-1}{b^3} \tag{1-124}$$

and E_1', E_2', α, β_o, E' and b are given by Equations (1-103), (1-105), (1-50), (1-51), (1-100) and (1-66), respectively. For lower dielectric constants the terms in E_2' in Equations (1-122) and (1-123) become small and $h(b) \simeq 2/b$; the dominant part of L is given by

$$L = 2E_1'\Lambda_o(1.601-\log_e b), \tag{1-125}$$

which goes through zero at b = 4.96 and is negative for larger values. Substitution of the numerical values for the physical constants--and noting that for 1:1 electrolytes $\mu = c$, $Z_+ = 1$ and $Z_- = -1$--in Equations (1-50), (1-51), (1-66), (1-97), (1-103), (1-105), (1-108) and (1-116) yields Equations (1-126)-(1-133), respectively:

$$\alpha = \frac{8.205\times10^5}{(DT)^{3/2}}, \tag{1-126}$$

$$\beta_o = \frac{82.49}{\eta(DT)^{1/2}}, \tag{1-127}$$

$$b = \frac{1.671\times10^{-3}}{aDT}, \tag{1-128}$$

$$K_A = (2.523\times10^{21})a^3\exp(b), \tag{1-129}$$

$$E_1' = \frac{2.943\times10^{12}}{(DT)^3}, \tag{1-130}$$

$$E_2' = \frac{4.333\times10^7}{\eta(DT)^2}, \tag{1-131}$$

$$\beta = \frac{1.671\times10^{-3}}{DT} \tag{1-132}$$

and

$$f_\pm^2 = \exp\left[\frac{-8.404\times10^6 c^{1/2}\gamma^{1/2}}{(DT)^{3/2}}\right]. \tag{1-133}$$

Equation (1-133) is obtained by squaring both sides of Equation (1-116) and replacing c with $c\gamma$ in the expression for τ (Equation (1-101)).

Fuoss, Onsager and Skinner stated that

> [Equation (1-120)] can be considered to be theoretically established. The principal contribution of this series of calculations is in fact to establish that retention of the Boltzmann factor without approximation leads directly to a term in $cf_\pm^2$ into the conductance equation, which in turn heuristically justifies the use of [Equation (1-120)] as the more general function of which [Equation (1-113)] is the limit. We shall refer to [Equation (1-120)] as the 1965 equation in order to distinguish it from earlier equations.

The conductance equation is a two-parameter equation since $\underline{L}$ and $\underline{K_A}$ are both functions of $\underline{b}$--that is, for a given solvent at a given temperature,

$$F(c,\Lambda,\Lambda_o,b) = 0. \tag{1-134}$$

However, the three parameter equation,

$$F(c,\Lambda,\Lambda_o,L,K_A) = 0, \tag{1-135}$$

yields smaller standard deviations for the difference between calculated and observed values of $\underline{\Lambda}$.

It should be mentioned that other methods have been proposed and developed for analyzing the general problem of conductance. Pitts (138) (139) (140), Falkenhagen, Leist and Kelbg (141) (142) (143), Robinson and Stokes (144) (145) (146), and Kremp, Kraeft and Ebeling (147) (148) (149), for example, have developed theories which give the concentration dependence of electrolyte conductance. Murphy and Cohen (150) (151) have modified the theory of Fuoss and Onsager and extended it so as to include asymmetric binary electrolytes. Murphy (152) has utilized recent advances in the theory of Brownian movement to derive the Fuoss-Onsager theory from the Liouville equation; he showed that the Fuoss-Onsager theory is sufficiently accurate to give the correct value of the conductance through the transcendental term, but it does not take into account some terms which affect the conductance to first order in the concentration. One theory of conductance in solution is based on the application of cluster expansion methods to Kubo's (153) general theory of transport processes; Friedman (154) (155) (156) (157) (158) (159) (160) derived the general equations, applied the theory to a simple model and then generalized the model. Recently Pikal (161)

developed a theory of mutual diffusion in a binary electrolyte using the charged sphere-in-continuum model and retaining the full Boltzmann exponential. From this procedure he obtained a term representing the effect of ion-pair formation as a natural consequence of the electrostatic interactions.

CHAPTER II

THE PROBLEM

Studies by Cunningham and Associates

Olson and Cunningham (162) found that the specific conductance of 0.01 molal lithium bromide in acetone is enhanced by thirty percent when sufficient bromosuccinic acid has been added to make the solution 0.2 molal with respect to the acid. They further found that when dimethyl bromosuccinate has been added in lieu of bromosuccinic acid the specific conductance is diminished by six percent and that when lithium perchlorate is substituted for lithium bromide the specific conductance decreases linearly as bromosuccinic acid is added. It was these observations which attracted the attention of Cunningham and he and his coworkers pursued his concern by amassing a great deal of data pertinent to the study of the electrolytic conductance of the lithium bromide-bromosuccinic acid-acetone system.

Bjornson (163) investigated the electrolytic conductance of systems comprising lithium halides and some carboxylic acids in acetone in order to determine the effect of the addition of successive increments of acid. He found that for most of the systems examined such additions of acid were accompanied by an anomalous rise in specific conductance. By means of a Fuoss plot he obtained values of 2.13×10^{-4} and 196.0 $\Omega^{-1}\ cm^2\ eq^{-1}$ for $\underline{K_D}$ and $\underline{\Lambda_o}$, respectively, for lithium bromide in acetone.

He suggested that in the case of the lithium bromide-bromosuccinic acid-acetone system the bromosuccinic acid is a stronger acid than hydrogen bromide and that hydrogen bromide would form in acetone. He proposed that the association of protons from bromosuccinic acid and bromide ions from lithium bromide would combine in the form of undissociated hydrogen bromide molecules--the removal of the ions would permit more lithium bromide and bromosuccinic acid to dissociate and thus the total number of ions would be increased leading to a larger specific conductance. Bailey (164) employed the same method to the hydrogen bromide-acetone system and got values of 1×10^{-6} and 110-120 Ω^{-1} cm^2 eq^{-1} for $\underline{K_D}$ and $\underline{\Lambda_o}$, respectively, for hydrogen bromide in acetone. Muller (165) measured viscosities, densities and dielectric constants of solutions composed of lithium bromide and some carboxylic acids in acetone. Mahan (166) also made density measurements on solutions of lithium bromide in acetone.

Related Studies

A survey of the literature indicates extensive research has been done on the electrolytic conductance of lithium bromide, the electrolytic conductance of acetone solutions and the electrolytic conductance in mixed solvents; consequently, this section consists of only those investigations pertaining to the electrolytic conductance of the lithium bromide-acetone system and the lithium bromide-bromosuccinic acid-acetone system.

A value for the equivalent conductance at infinite dilution for lithium bromide in acetone was first calculated in 1905 by Dutoit and Levrier (167) for 18 °C: 166 Ω^{-1} cm^2 eq^{-1}. The graphical method of

Equation (1-11) was applied to their data in 1913 by Kraus and Bray (25) who obtained values of 5.7×10^{-4} for K_D and 165 Ω^{-1} cm^2 eq^{-1} for Λ_o. Deviations from the mass action law (nonlinearity in the graph) become appreciable at concentrations of about 10^{-3} molar. Both groups pointed out that measurements in acetone are liable to be seriously affected by several sources of error, including the presence of solvent impurities and exposure to light. A conductance solvent correction of 21 percent was applied to their most dilute solution.

In 1910 Serkov (168) determined the conductance of several salts (including lithium bromide) at 25 °C in water, methanol, ethanol, acetone and binary mixtures of these solvents, reporting a value of 144 Ω^{-1} cm^2 eq^{-1} for Λ_o for lithium bromide in acetone. He found that, contrary to the other mixtures, no parallelism exists between conductance and fluidity in mixtures of which one component is acetone and concluded that when the surveyed ionophores are dissolved in acetone, solvates are formed and that the complexity of the solvates increases as Λ_o for the ionophores decreases.

In 1939 Dippy, Jenkins and Page (169) found that the phoreogram for lithium bromide in acetone at 25 °C contains an inflection point and were unable to get Λ_o by extrapolation. It would appear, however, from inspection of their phoreogram that Λ_o is in the proximity of Serkov's value rather than that of Kraus and Bray. They noted that although different batches of acetone had different specific conductances the data points of the phoreogram lay uniformly on a smooth curve and they considered it as evidence of the satisfactory nature of the solvent correction employed.

Reynolds and Kraus (103) procured conductance data for fourteen different salts in acetone at 25 °C and used the Fuoss method to calculate their equivalent conductances at infinite dilution. Among the salts were tetra-n-butylammonium triphenylborofluoride, tetra-n-butylammonium picrate, lithium picrate and tetra-n-butylammonium bromide for which they obtained values of 134.2 Ω^{-1} cm^2 eq^{-1}, 152.4 Ω^{-1} cm^2 eq^{-1}, 158.1 Ω^{-1} cm^2 eq^{-1} and 183.0 Ω^{-1} cm^2 eq^{-1}, respectively, for Λ_o. They then generated ionic equivalent conductances at infinite dilution by the method of Fowler using tetra-n-butylammonium triphenylborofluoride as the reference electrolyte. Application of Kohlrausch's law of the independent migration of ions produces values of 72.8 Ω^{-1} cm^2 eq^{-1}, 115.9 Ω^{-1} cm^2 eq^{-1} and 188.7 Ω^{-1} cm^2 eq^{-1} for λ_o^+ for lithium ion, λ_o^- for bromide ion and Λ_o for lithium bromide, respectively.

In 1953 Olson and Konecny (170) studied the conductance of lithium bromide in acetone-water mixtures at 25 °C and 35 °C. They calculated K_D and Λ_o in the acetone-rich solvents by the Fuoss method, Λ_o in the water-rich solvents by extrapolation of the phoreogram and a, the sum of the ionic radii, by Bjerrum's method. Their results for 25 °C are summarized in Table I. (It should be noted that 0.45 weight percent water corresponds to 0.25 molal water.) It is seen from Table I that as the water content increases, K_D increases, Λ_o decreases but then undergoes an increase and a increases from slightly less than the sum of the crystal ionic radii to the sum of the fully hydrated radii.[1] Extrapolation of their data for Λ_o to zero water content would not be

[1]The crystal ionic radii of lithium ion and bromide ion are 0.68 Å and 1.96 Å, respectively (171).

reliable because of the large concave upward negative slope; however, it would appear to lead to a value in the vicinity of 220 Ω^{-1} cm^2 eq^{-1}. Similar extrapolations of values for K_D and a yield 2.0×10^{-4} and 2.2 Å, respectively.

TABLE I

CONDUCTANCE DATA FOR LITHIUM BROMIDE IN AQUEOUS ACETONE

Weight % H_2O	K_D	Λ_o ($\Omega^{-1}cm^2eq^{-1}$)	a (Å)
0.45	2.56×10^{-4}	206.6	2.28
2.89	8.52×10^{-4}	159.2	2.50
5.35	1.76×10^{-3}	138.9	2.62
12.48	9.5×10^{-3}	102.6	3.33
23.67	$8. \times 10^{-2}$	77.9	6.17
57.8		64.5	
84.0		86.2	
100.0		118.5	

Source: Olson and Konecny (170).

Two years later Nash and Monk (172) also measured conductances at 25 °C using aqueous acetone (12.5 weight percent water) as the solvent. For K_D they obtained values of 1×10^{-3} and 6×10^{-3} for lithium bromide and hydrogen bromide, respectively, by the Davies method and 101.1 Ω^{-1} cm^2 eq^{-1} and 117.1 Ω^{-1} cm^2 eq^{-1} for Λ_o for lithium bromide and hydrogen bromide, respectively, by the Fuoss method.

Olson, Frashier and Spieth (173) noted that the addition of lithium bromide to a solution of the dimethyl ester of ℓ-bromosuccinic acid

in acetone causes racemization of the ester and that the specific rate of racemization depends upon the concentrations of the lithium bromide and of the ester. They used the results of Kraus and Bray to calculate concentrations of the lithium bromide species in solution. Konecny (174) re-examined the rate data using dissociation constants obtained by extrapolation of the results of Olson and Konecny to zero water content; this led to a different interpretation which gives no indication of a lithium bromide catalyzed path--the rates are proportional to the concentration of bromide ions.

A summary of the values which have been obtained for Λ_o and K_D for lithium bromide in acetone is presented in Table II. There is an obvious discrepancy in these values. The inconsistencies may be in part a consequence of the presence of water.

TABLE II

SUMMARY OF CONDUCTANCE DATA FOR LITHIUM BROMIDE IN ACETONE

Investigators	Λ_o ($\Omega^{-1}cm^2eq^{-1}$)	K_D	Comment
Dutoit and Levrier (167)	166		18 °C
Serkov (168)	144		25 °C
Kraus and Bray (25)	165	5.7×10^{-4}	18 °C, Equation (1-11) with data from Dutoit and Levrier
Reynolds and Kraus (103)	188.7		25 °C, combined Fuoss and Fowler methods
Olson and Konecny (170)	220	2.0×10^{-4}	25 °C, estimated from Fuoss method in aqueous acetone
Bjornson (163)	196.0	2.13×10^{-4}	25 °C, Fuoss method

The Proposal

It is the purpose of this study to determine whether or not the electrolytic conductance of the lithium bromide-bromosuccinic acid-acetone system can be described by the Fuoss-Onsager-Skinner equation (FOS equation)--Equation (1-120)--by treating the system as lithium bromide in a mixed solvent, and to establish values for $\underline{\Lambda_o}$ and $\underline{K_A}$ for lithium bromide in anhydrous acetone with the same equation. The equation requires knowledge of the concentration and corresponding equivalent conductance in conjunction with the dielectric constant and viscosity of the solvent and the temperature; that is,

$$F(c,\Lambda,D,\eta,T) = 0. \qquad (2\text{-}1)$$

The essential data are to be compiled from the data acquired from the experimental portion of this study and those accumulated by Cunningham and coworkers. The experimental portion consists of measuring the electrical resistance at 25 °C of solutions of varying amounts of lithium bromide in acetone, lithium bromide in bromosuccinic acid and acetone, and lithium bromide in dimethyl bromosuccinate and acetone.

This is an extremely complicated system for such a study inasmuch as it is a three component system consisting of an ionophore (lithium bromide) and an ionogen (bromosuccinic acid) in a smenogenic solvent (acetone). Further, the solvent has a high affinity for water and a high vapor pressure at 25 °C.

CHAPTER III

REAGENTS USED FOR THE PREPARATION OF THE CONDUCTANCE SOLUTIONS

If electrolytic conductance data are to be meaningful knowledge of the composition of the system is essential. This necessitates having as nearly pure materials as possible and an estimate of their purity. This work demanded that the species under investigation--acetone, bromosuccinic acid, dimethyl bromosuccinate and lithium bromide--be as nearly pure and reproducible as possible. It also required potassium chloride and water of high purity for the calibration of the conductance cell.

Acetone

Several batches of very nearly anhydrous acetone were prepared by the method of Howard and Pike (175). A two-dm^3 Pyrex round bottom flask with a 24/40 standard tapered outer joint was cleaned, rinsed with acetone and dried at 120 °C. Approximately 200-250 g of 1/16-in synthetic zeolite pellets (Linde Type 5A molecular sieve) was placed in the flask and 1.5 dm^3 of acetone (Fisher certified ACS) was added. The flask was stoppered and stored in a dark cabinet for a minimum of two days, during which time the contents were swirled and mixed

intermittently.[1] It was then placed in a Glass-Col metal covered heating mantle (controlled by a Variac powerstat) and connected to a Pyrex fractionating distillation column which had been flushed with acetone and purged with nitrogen. The nitrogen had been passed through a 1.2-m length of 32-mm Pyrex glass tubing which was filled with indicating silica gel.

The distillation column was approximately one m long and 2-3 cm in diameter; it was packed with glass helices and sealed inside a silvered vacuum jacket which had an outside diameter of about 10 cm. The column was connected to a Pyrex distillation head by a 24/40 standard tapered Pyrex glass joint. The side of the water cooled condenser in the head had four vertical ribs so spaced that the ratio of the amount of liquid dropping from between two adjacent ribs to the total amount of liquid dropping from the condenser was 1:1, 1:5, 1:5 and 1:10. The condenser could be rotated in such a manner that these various fractions of the condensed liquid dropped into the receiving cup and thus the reflux ratio could be regulated. The vent was connected to a drying tube which was filled with indicating silica gel. A Pyrex glass

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[1]Acetone which had been left in contact with molecular sieves for several months was yellow. Apparently the sieves catalyze the same reaction that occurs when acetone is saturated with hydrogen chloride and allowed to stand for several days. A proposed mechanism involves addition of the enol form of acetone to the conjugate acid of acetone followed by a normal acid-catalyzed dehydration reaction to form 4-methyl-3-penten-2-one (mesityl oxide); the mesityl oxide reacts with the acetone in a similar manner to produce 2,6-dimethyl-2,5-heptadien-4-one (phorone) (176). The boiling points of acetone, mesityl oxide and phorone are 56.2 °C, 130-1 °C and 197 °C, respectively (171). Distillation of the yellow acetone yielded a colorless distillate whose properties were essentially the same as the other acetone used for conductance measurements.

adapter was constructed so that a Pyrex flask with a 24/40 standard tapered inner joint could be used for the receiver. This was done to allow the acetone to be poured from the receiver without coming in contact with the lubricant. A minimum of lubricant (Dow Corning stopcock grease--silicone lubricant) was used on all joints.

The acetone was refluxed and then distilled with a reflux ratio of 1:1. After 250 cm^3 had distilled a new receiver was connected and one dm^3 of acetone collected in a one-dm^3 Pyrex Erlenmeyer flask--this was the acetone used. The flask, which had an inner 24/40 standard tapered top, was stoppered immediately with an outer Pyrex 24/40 standard tapered cap and stored in the dry box; it was opened only therein.

One batch of the acetone had a specific conductance of 3×10^{-9} Ω^{-1} cm^{-1} and the others 2×10^{-8} Ω^{-1} cm^{-1}. The one with the lowest specific conductance was prepared from the acetone which had remained in contact with molecular sieves for several months; the others were not. The specific conductance of the distilled acetone increased upon standing in the Pyrex glass flask. For this reason all solvents were prepared from freshly distilled acetone.

Bjornson (163) dried acetone by adding anhydrous calcium sulfate and allowing it to stand. The acetone was then distilled from the mixture under vacuum at room temperature. The vapor was passed through a column containing phosphorous pentoxide and condensed in a flask immersed in a dry ice-acetone bath.

Bailey (164) prepared acetone in essentially the same manner as was done for this work. He prepared one batch which had a specific conductance of 1.08×10^{-7} Ω^{-1} cm^{-1} and a density of 0.7839 g cm^{-3} and another batch with a specific conductance of 6.9×10^{-8} Ω^{-1} cm^{-1} and a

density of 0.7838 g cm^{-3}. Bailey saturated samples of the dried acetone with cesium fluoride and obtained the specific conductance of each sample. He compared these data with conductance data for Bjornson's acetone which had been saturated with cesium fluoride. This procedure was used by both because Mysels (177) had suggested that the conductance of saturated solutions of a salt such as cesium fluoride would be a simple and sensitive method for determining traces of moisture in acetone. Bailey's cesium fluoride-acetone solutions had a lower specific conductance than those of Bjornson, indicating a lower moisture content. Bailey compared his data with Mysels' data and found that "the acetone appeared to be very nearly anhydrous."

Sears, Wilhoit and Dawson (178) obtained a value of 2×10^{-8} Ω^{-1} cm^{-1} for the specific conductance of acetone.[2] Reynolds and Kraus (103) got an order of magnitude lower; their acetone was dried by agitation over calcium chloride and then distilled twice from activated alumina pellets. Dippy and Hughes (180) attempted to reproduce these results by using the same method but obtained values for the specific conductance which were of the order of magnitude of 10^{-8} Ω^{-1} cm^{-1}. They obtained consistent values for the equivalent conductance of potassium iodide in independent batches of acetone whose specific conductances ranged from 2.09×10^{-8} Ω^{-1} cm^{-1} to 2.36×10^{-8} Ω^{-1} cm^{-1} and concluded that there is no serious objection to a moderate total solvent correction.

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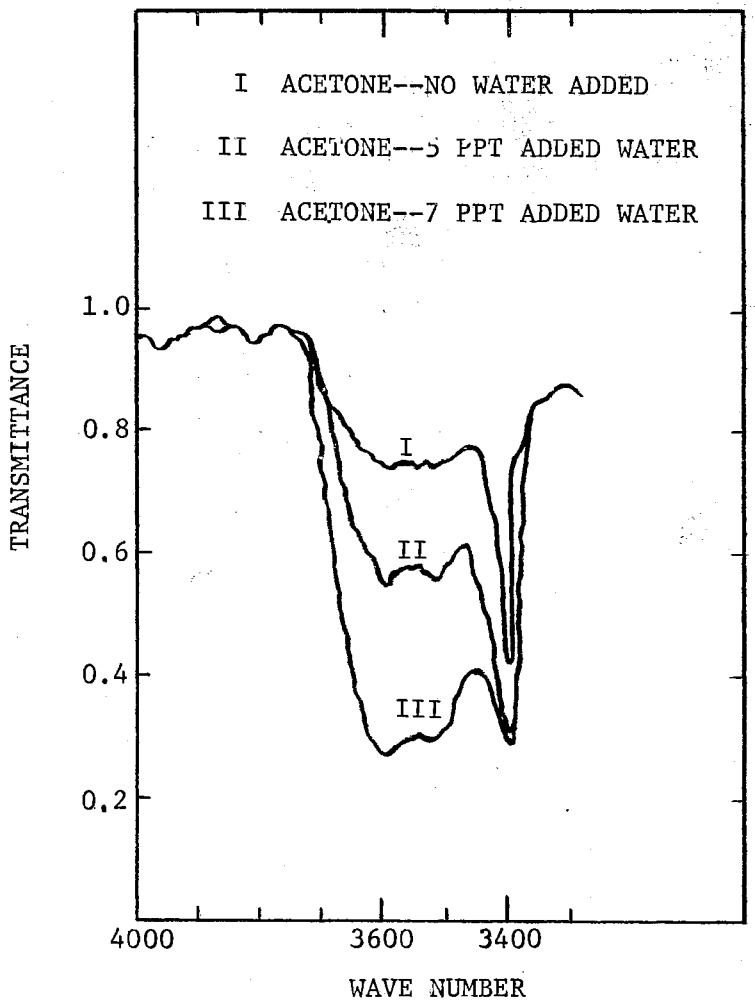
[2]This is the reference cited for the literature value of the specific conductance of acetone in A Survey of Non-Aqueous Conductance Data (179).

The infrared spectrum of liquid reagent grade acetone shows a sharp absorption band at a wave number of 3400 cm^{-1} and a broader band at 3600 cm^{-1}. Lucchesi (181) found that this absorption increases with increasing water concentration in acetone. This band is considered to be a result of intermolecular hydrogen bonding between acetone and water. Lucchesi purified acetone by the method of Shipsey and Werner (182) and also by repeated fractional distillation of commercial acetone. As is evident from Figure 1, which shows a reproduction of the spectra obtained by Lucchesi, he was unable to eliminate the band. He concluded that the driest acetone he prepared had about 2.5 parts per thousand by volume which is approximately 0.1 molal water.

The infrared spectrum of the acetone used in this work was obtained both before and after distillation. The first few spectra were obtained with a Beckman model IR7 infrared spectrophotometer. However, it was learned that that much resolution was not required. Throughout the project the majority of the infrared spectra was procured with a Beckman model IR8 infrared spectrophotometer. In all cases a sodium chloride cell was utilized with air as the reference; the cell was filled in the dry box with a syringe following the usual precautions concerning the cleansing and storing of such a cell. Prior to distillation the acetone had an absorption band at 3600 cm^{-1}. Figure 2, which was reproduced from the spectra recorded by the spectrophotometer, shows clearly that distillation did not simply reduce the band--it expunged it.

It is not claimed that the acetone is anhydrous; however, the infrared spectrum and specific conductance imply that it is as nearly anhydrous as is possible with present means and knowledge. It is humbly alluded to by the author as "The World's Driest Acetone."



Source: Lucchesi (181).

Figure 1. Lucchesi's Spectra of Acetone-Water Mixtures in the 3600 cm^{-1} Region

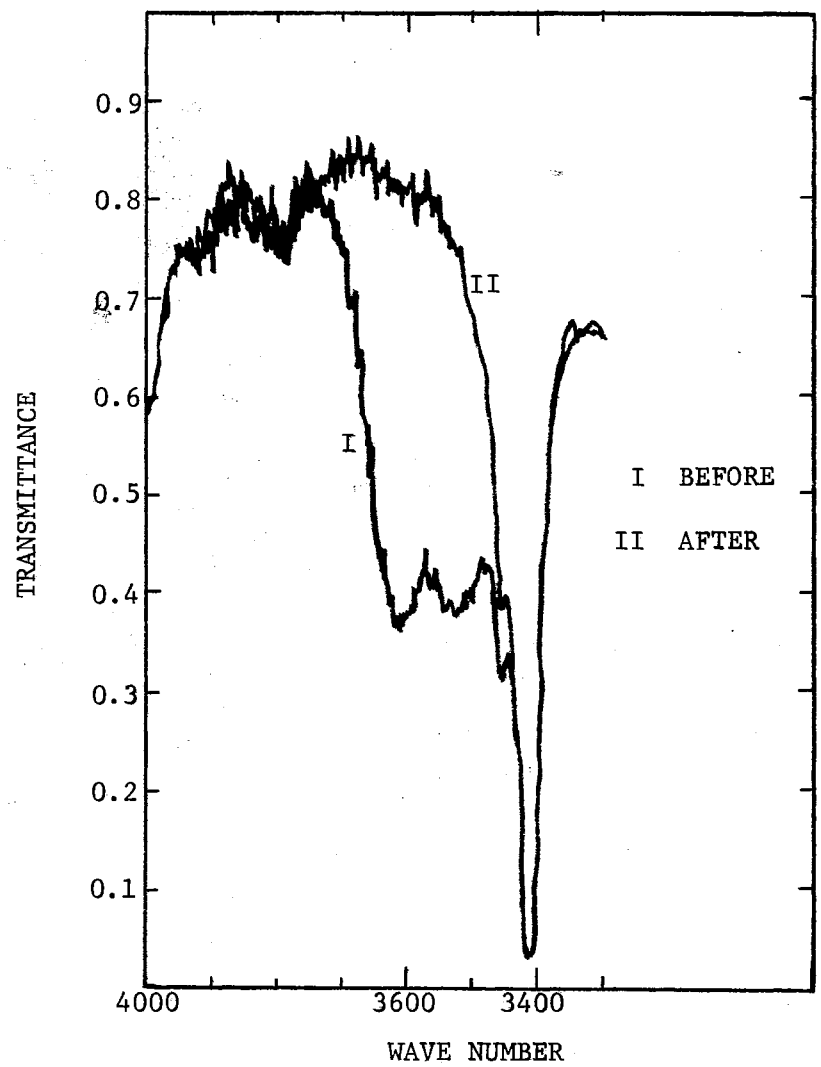


Figure 2. Spectrum of Acetone in the 3600 cm^{-1} Region Before and After Distillation

Bromosuccinic Acid

Bromosuccinic acid was purchased from K & K Laboratories, Inc., Plainview, New York. The manufacturer asserted a purity of 99 percent. A portion of the snow white powder was transferred to a clean dry weighing bottle and placed in the drying oven at 110 °C for two hours. The weighing bottle was stoppered and put in the dry box to cool; it was stored in the dry box and opened only therein. This bromosuccinic acid was used without further treatment in the preparation of the conductance solutions.

The melting point was determined with a Thomas Hoover capillary melting point apparatus. A capillary tube containing a sample of the bromosuccinic acid was situated in the apparatus and the temperature was raised rapidly. The compound melted smoothly in the range of 160-165 °C; the capillary was removed and the compound solidified in the tube. A second sample in another capillary tube was put in the apparatus and heated slowly. At about 161 °C it began to melt and then part of it began to rise in the tube, but did not appear to melt anymore. The white solid in the bottom began to rise at about 174 °C, but did not melt. At 184 °C the capillary tube--still containing the white solid--was displaced from the apparatus. The capillary containing the first sample was placed in the apparatus while the oil was at a temperature of approximately 180 °C; the contents liquified immediately. The literature value for the melting point of bromosuccinic acid is 160-161 °C (171). Dictionary of Organic Compounds (183) states, "Heat above m.p. → fumaric acid." Conceivably when the bromosuccinic acid was heated rapidly it just melted, but when it was heated slowly

fumaric acid was formed by the elimination of hydrogen bromide. As the gas was formed it pushed the solid up the capillary tube. The literature value for the melting point of fumaric acid is above 250 °C (171).

Kinneberg of the Biochemistry Department of Oklahoma State University procured the mass spectrum of a sample of the bromosuccinic acid with a prototype of the LKB-9000 combination gas chromatograph-mass spectrometer.[3] There was no peak corresponding to the parent compound. Of the most abundant peaks, the largest mass to charge ratio corresponded to the parent compound minus water, the next largest to the parent compound less water and carbon monoxide, the next to hydrogen bromide and the next to atomic bromine. There were also fragments matching carbon monoxide and water. No impurities could be identified. In particular, there were no peaks corresponding to fragments containing two bromine atoms. The mass spectrum for bromosuccinic acid was not found in the literature, but that for succinic acid was (185). The mass spectrum for the bromosuccinic acid was quite analogous to that for succinic acid (for example, no parent peak).

A portion of the acid was put in a screw cap vial and sent to Galbraith Laboratories, Inc., Knoxville, Tennessee, for hydrogen and carbon analyses. They reported values of 2.50 percent hydrogen and 24.57 percent carbon; this gives a molar ratio for hydrogen to carbon of 1.21 to 1.00. If four carbon atoms are assumed to be present, the analysis gives a ratio of five hydrogen atoms to four carbon atoms, which is in agreement with the formula for bromosuccinic acid. The calculated values are 2.56 percent hydrogen and 24.39 percent carbon,

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[3]This instrument has been described by Waller (184).

which yield absolute errors of minus 0.06 percent and plus 0.18 percent, respectively. The absolute errors for both hydrogen and carbon are well within the tolerance limits of ±0.4 percent set by the Journal of Organic Chemistry.

Dimethyl Bromosuccinate

Eisenbraun, Morris and Adolphen (186) prepared dimethyl succinate by the diazomethane method. Morris directed and aided the author in the synthesis of dimethyl bromosuccinate using the same method. Diazomethane was prepared using EXR-101 (E. I. du Pont de Nemours & Company, Inc.), which is NN'-dinitroso-NN'-dimethyl terephthalamide with an inert filler. The method was essentially that of Moore and Reed (187).[4]

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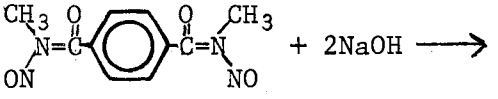
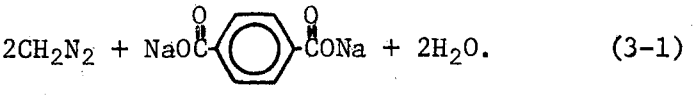
[4]Diazomethane is toxic and explosive. Precaution must be used in its preparation and handling. Several batches were prepared using the apparatus and the following procedure of Eisenbraun and coworkers: In a 500 cm^3 flask, a solution of 2.4 g of sodium hydroxide in 20 cm^3 of water, 50 cm^3 of carbitol (diethylene glycol mono ethyl ether) and 150 cm^3 of diethyl ether was cooled to 0 °C; then 7.1 g of EXR-101 was added at one time. The solution was stirred magnetically and the reaction mixture warmed slowly. The evolution of diazomethane became apparent at 15-20 °C. In the 30-40 °C range the diazomethane and diethyl ether distilled; the condensed distillate was bright yellow. (During this reaction the receiver was cooled with dry ice; diethyl ether was added from a dropping funnel whenever the amount of diethyl ether in the reaction flask became small. The lower layer became white and viscous during the latter part of the reaction and stirring became more difficult.) The reaction was assumed complete when the yellow color of the EXR-101 in the reaction flask and of the distilling diethyl ether disappeared. An ether solution containing about two g of diazomethane was obtained. The equation for the reaction is





(3-1)

A 25.3 g sample of the same bromosuccinic acid as was used in the preparation of the solvents was placed in 200 cm^3 of diethyl ether. Not all of the bromosuccinic acid dissolved. The yellow solution of diazomethane in diethyl ether was added to the mixture, whereupon the combined solution became colorless, gas (nitrogen) was evolved and the excess bromosuccinic acid dissolved.[5] The total volume of the solution was reduced by removing the diethyl ether with an aspirator and then more diazomethane was added; this step was repeated until the bubbling of the gas was very slow. The excess diethyl ether was removed by means of an aspirator. The remaining oil had a very slight yellow tinge and was clear; however, during the final part of the ether distillation it became tan or brownish in color. The oil was then distilled under vacuum in a range of 45-49 °C. (The literature value for the boiling point of dimethyl bromosuccinate is 110 °C at 10 Torr (183).) The temperature appeared to be varying as a consequence of fluctuations in pressure. (A McLeod gauge was in the vacuum system and the following was observed: 49 °C at 0.1 Torr and 45 °C at 0.08 Torr.) As the distillation continued the pot became cloudier and ultimately most of the contents solidified; the color of the solid was brown-tan. About 13 g of the distillate--less than half of the theoretical yield--was obtained. This clear colorless oil was transferred to the screw capped bottle in which it was kept. It was this dimethyl bromosuccinate which was used in the preparation of the conductance solutions.

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[5]The equation for the reaction is

$$HCO_2CHBrCH_2CO_2H + 2CH_2N_2 \longrightarrow CH_3CO_2CHBrCH_2CO_2CH_3 + 2N_2\uparrow. \qquad (3\text{-}2)$$

A portion of the dimethyl bromosuccinate was treated by means of thin layer chromatography using benzene as the solvent and a symmetrical single spot was obtained which indicates either a pure compound or no separation with this particular solvent.

The mass spectrum of a portion of the dimethyl bromosuccinate was produced by Kinneberg (Biochemistry Department, Oklahoma State University) with the same instrument as was used for determining the mass spectrum of the bromosuccinic acid. In general, the spectrum resembled a picket fence--it had a very small peak corresponding to the parent compound, but none to a dibromo compound. The mass spectrum for dimethyl bromosuccinate was not found in the literature, but that for dimethyl succinate was (185). It too looks like a picket fence and has a small peak corresponding to the parent compound.

The closed end of a melting point capillary tube was heated and the open end dipped into a small amount of the ester; while the tip was still immersed in the liquid the closed end was surrounded by dry ice. After the sample was drawn into the tube it was quickly placed in the centrifuge. The open end was then sealed with a flame and the sealed sample dispatched to Galbraith Laboratories, Inc., Knoxville, Tennessee, for hydrogen and carbon analyses. They reported values of 4.19 percent for hydrogen and 32.15 percent for carbon. These values give an absolute error of plus 0.16 percent for hydrogen and plus 0.13 percent for carbon when compared with the calculated values for dimethyl bromosuccinate of 4.03 percent and 32.02 percent, respectively. The tolerance levels set by Journal of Organic Chemistry are ±0.4 percent. The experimental values yield a molar ratio for hydrogen to carbon of 1.55

to 1.00. If one assumes six carbons are present, the analysis results in a ratio of nine hydrogen atoms to six carbon atoms, which is in agreement with the formula for dimethyl bromosuccinate.

Lithium Bromide

Reagent grade anhydrous lithium bromide powder (Matheson, Coleman and Bell) was transferred directly from the commercial bottle to a weighing bottle. The weighing bottle, with its ground glass stopper lying on its side on top of it, was placed in a vacuum oven (Weber electric vacuum oven) and a 250-cm^3 beaker was inverted over it. Between the oven and vacuum pump (Welch Duo Seal model 1402) was a three-way stopcock which was connected to a cylinder of nitrogen. The oven was evacuated and the lithium bromide was secured under vacuum for one day at room temperature followed by one day at 100-120 °C. After the oven had been turned off, the vacuum was released by turning the stopcock so as to pass nitrogen into the oven. The oven was opened at 80 °C and the weighing bottles were stoppered and quickly transferred to a vacuum desiccator containing molecular sieves and indicating silica gel. The desiccator was evacuated and stored in the dry box--it was opened only in the dry box, as was the weighing bottle.

Potassium Chloride

Potassium chloride (Fisher certified ACS) was transferred directly from the commercial bottle to a weighing bottle which was placed in a drying oven at 110 °C for one day. The weighing bottle was then put in a desiccator containing molecular sieves and indicating silica gel.

The potassium chloride cooled to room temperature in the desiccator and was stored there until used.

Water

De-ionized water from the laboratory supply was piped directly into a Pyrex glass still (Corning model AG-1a) and distilled into a polyethylene vessel. This water was transferred to a polyethylene bottle in which it was kept until used. The specific conductance of the water was determined as described in Chapter IV and found to be $1 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$.

Desiccants

All molecular sieves used throughout the work were Linde Type 5A 1/16-in pellets, all indicating silica gel was Sargent silica gel indicating 6-16 mesh and all nitrogen was Linde high purity dry lamp grade.

CHAPTER IV

APPARATUS FOR THE CONDUCTANCE MEASUREMENTS

A Wheatstone bridge can be used to measure the resistance--and, consequently, the conductance--of a conducting system. A schematic diagram of a Wheatstone bridge is shown in Figure 3, in which S is a source of electric current and D is a current detector. Part of the current passes through the unknown resistance, R_x, and the adjustable known resistance, R_r. The remainder of the current passes through the known resistances, R_a and R_b, provided the bridge has been balanced by adjusting R_r so no current passes through D. It can be shown that under these conditions

$$R_x = R_r\left(\frac{R_a}{R_b}\right). \tag{4-1}$$

It is an easy matter to measure the electrical resistance of a metallic conductor with such an apparatus. The process for the measurement of the resistance of an electrolytic conductor--particularly a non-aqueous electrolytic conductor--is much more complex. An electrolytic conductor must be placed in a container and it must be in contact with electrodes (metallic conductors). This connotes a chemical reaction occurring at the interface of the electrolytic and metallic conductors, resulting in polarization of the electrode, which invalidates any measurement of the resistance. In order to minimize this effect alternating

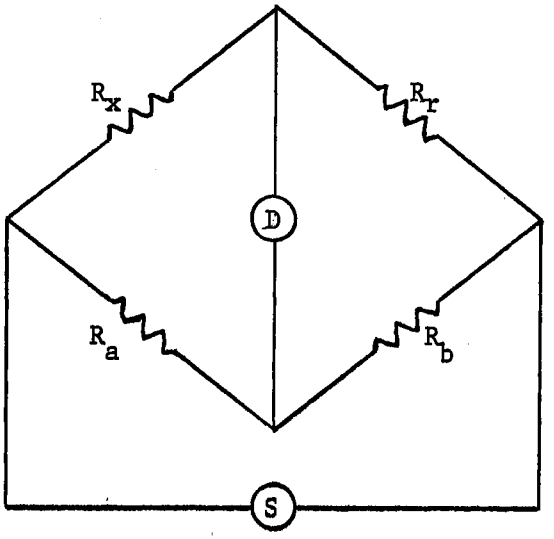

Figure 3. Schematic Diagram of a Wheatstone Bridge

current is generally employed.[1] Unfortunately, the utilization of alternating current introduces other complications into the resistance measurements because the potential difference and the current in each arm of the bridge have to be considered. Both are time dependent and may be out of phase with respect to each other. In order to balance the bridge the following condition must be met in addition to that of Equation (4-1):

$$\theta_x + \theta_c = \theta_a + \theta_b, \qquad (4\text{-}2)$$

in which θ is the phase angle by which the voltage leads the current. Equation (4-2) in effect balances the reactance which is due to inductance and capacitance in the circuit (189).

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[1]It has been shown that direct current conductance measurements are capable of the same precision as alternating current measurements (188).

Obviously the design of the conductance bridge and the conductance cell is of great importance if errors due to reactance are to be eliminated. Many modifications of Wheatstone bridges for measuring electrolytic conductance have been described and discussed in the literature. Among them are those of Washburn and coworkers (190) (191), Taylor and Acree (192) (193) (194), Morgan and Lammert (195), Jones and associates (196) (197), Shedlovsky (198), Dike (199), Luder (200), Ives and colleagues (201) (202), and Wolff (203).[2] Similarly, a variety of conductance cells has been described in the literature; much of the published work was done by the people just mentioned (52) (204) (205) (206) (207). Inasmuch as the temperature coefficient of conductances is about two percent per degree Celsius it is critical to have the cell thermostated. The general principles of thermostat design are discussed by Lewin (208). Also, in the case of nonaqueous systems it is necessary to have a means of preparing solutions in the absence of moisture. In view of the importance of these factors, a detailed description of the conductance bridge, conductance cell, controlled-temperature bath and dry box follows.

Conductance Bridge

All electrical resistances were measured with an electrolytic conductivity bridge (Leeds and Northrup model 4666). It is a standard impedance bridge which has been designed for precision resistance measurements of electrolytic solutions. Capacitors in the arms of the bridge

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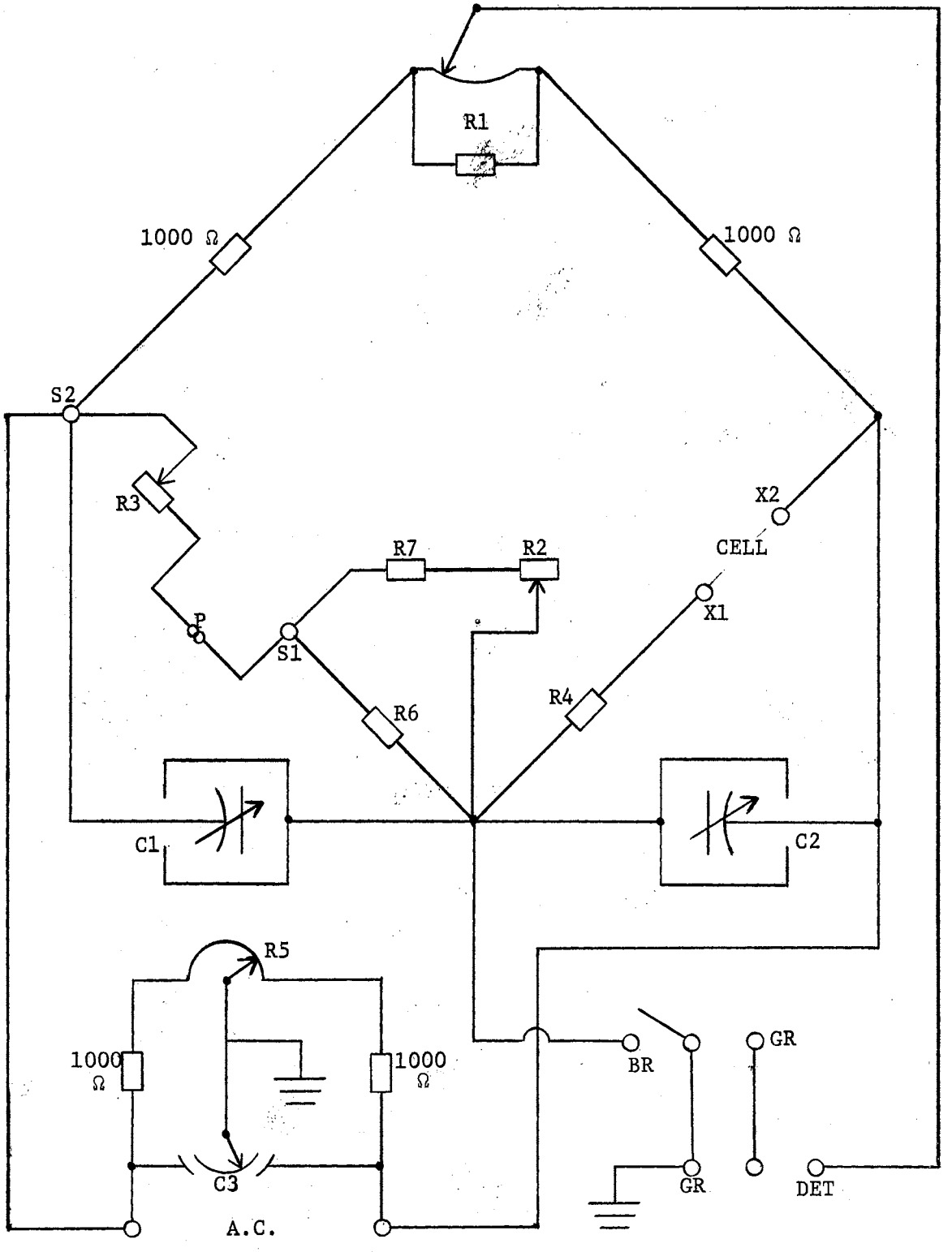
[2]Luder (200) pointed out that there were 48 papers on alternating current bridge methods published in 1932 alone.

compensate for capacitance of the conductance cell and provide phase angle balance. This conductivity bridge has been described by Dike (199); it was constructed using specifications set forth by Jones (196) and is referred to as a Jones bridge. A schematic diagram of the bridge circuit for making alternating current measurements is shown in Figure 4. The rheostat arm consisted of five 10 000-Ω knife switch operated resistors and five decade resistors (1000, 100, 10, 1, 0.1 Ω) for a total of 60 011 Ω; these composed R3 in Figure 4. The range could be extended by connecting external resistors to binding posts provided on the bridge. The rheostat arm included a slide wire (R2 in Figure 4) which permitted the bridge to be balanced with a precision of 0.001 Ω. The ratio arm (R1 in Figure 4) consisted of two 1000-Ω resistors which were matched in temperature coefficient and phase angle. An adjustable capacitor (C1 in Figure 4) with a range of 50 to 1000 pF was connected across the rheostat arm and one with a range of 10 to 120 pF (C2 in Figure 4) was connected in parallel with the resistance being determined. Capacitor C2 functioned as a fine adjustment for C1; it also rendered it possible to bring about a balance when the effective capacitance of the arm with the unknown resistance was less than the capacitance of C1 at its minimum value. Additional capacitance could be obtained by connecting an external capacitor across the rheostat arm at S1 and S2 in Figure 4. In some measurements in this work a polystyrene decade capacitor (General Radio Company type 1419-A) was used. The ground connection was a modified Wagner type (C3 and R5 in Figure 4). Capacitors C1 and C2 and the ground connection assembly were shielded. In addition, the front of the instrument had a grounded metal shield to reduce the effects of body capacitance to a minimum.



Source: Leeds and Northrup Direction Manual for the Model 4666 Electrolytic Conductivity Bridge

Figure 4. Schematic Diagram of the Jones Bridge Circuit When Using Alternating Current

The audio-frequency source was a General Radio Company type 1311-A audio oscillator and it was used with the frequency regulated at 1000 Hz and the output at about five V. The output for the oscillator was connected to an input transformer (Leeds and Northrup 019200). A double lead from this transformer was attached to terminals on the bridge at A.C. in Figure 4 and a single lead to the horizontal input of the oscilloscope (Heathkit model O-11), which constitutes part of the detecting device. The horizontal frequency selector and synchronization selector of the oscilloscope were set for external input. The vertical and horizontal positions and horizontal gain were adjusted so as to get a wide (horizontally) and centered display and the vertical input was set at a factor of one. The remainder of the detector circuit consisted of a high gain low noise tuned amplifier and null detector (General Radio Company type 1232-A) and an output transformer (Leeds and Northrup 019201). The output of the null detector was joined to the vertical input of the oscilloscope. The null detector was used with the linear meter and the frequency set for the 200-2000 Hz range with the filter tuning fixed at 10. The output transformer was connected to the input of the null detector; the transformer was wired to the bridge at the terminals DET and also grounded at GR in Figure 4. All external leads were shielded. The bridge was grounded by fastening the lead from GR to a metal rod driven through the floor into the ground. The oscillator and oscilloscope were powered by the 110 V-60 Hz line.

The bridge, null detector and external capacitor were on a firm table which minimized vibrations. The oscilloscope was on a wooden box, which was about 45 cm high, placed on the table. The screen of the oscilloscope tube was hooded so that the image could be seen better and

when measurements were being obtained the switch to the lights in the vicinity was opened. The two transformers were as far from the bridge as the leads permitted and were about one m from each other. The oscillator and null detector were as far from their respective transformers as allowed by the leads.

All connections and relative positions among the bridge and auxiliary components were made in accordance with the recommendations of the manufacturer; these connnections and positions are crucial. The arrangement of the apparatus, including the controlled temperature system, is shown in Figure 5.

Before the necessary resistance measurements were made the ratio arm and slide wire were checked against standard resistors and adjusted according to the calibration procedure outlined by the manufacturer. The ratio arm was fixed so that the ratio of the two resistances was 1.00000 to one; this means by Equation (4-1), that when the bridge is balanced the resistance of the unknown is the same as that of the rheostat arm, $\underline{R_r}$.

Many resistance measurements were made on a variety of metallic and electrolytic conductors. This was done primarily for two reasons--to learn the best combinations to be used and to develop the necessary technique for making the measurements. Among the items noted from these preliminary measurements were the following: (1) For small resistances the slope of the oscilloscope image was more sensitive to changes in capacitance and the vertical spread to changes in resistance; the converse was true for large resistances. This change in response occurred gradually as the resistance was increased. (2) The effect of body capacitance became quite prominent in some measurements. To minimize

1. Refrigerator Temperature Controller
2. Refrigerator Compressor
3. Thermister
4. Circulation Pump
5. Refrigeration Bath
6. Audio Oscillator
7. Input Transformer
8. Output Transformer
9. Null Detector
10. Oscilloscope
11. Capacitor
12. Bridge
13. Resistor
14. Constant Temperature Bath Controller
15. Constant Temperature Bath
16. Cell
17. Circulation Motor and Fan
18. Rubber Tubing

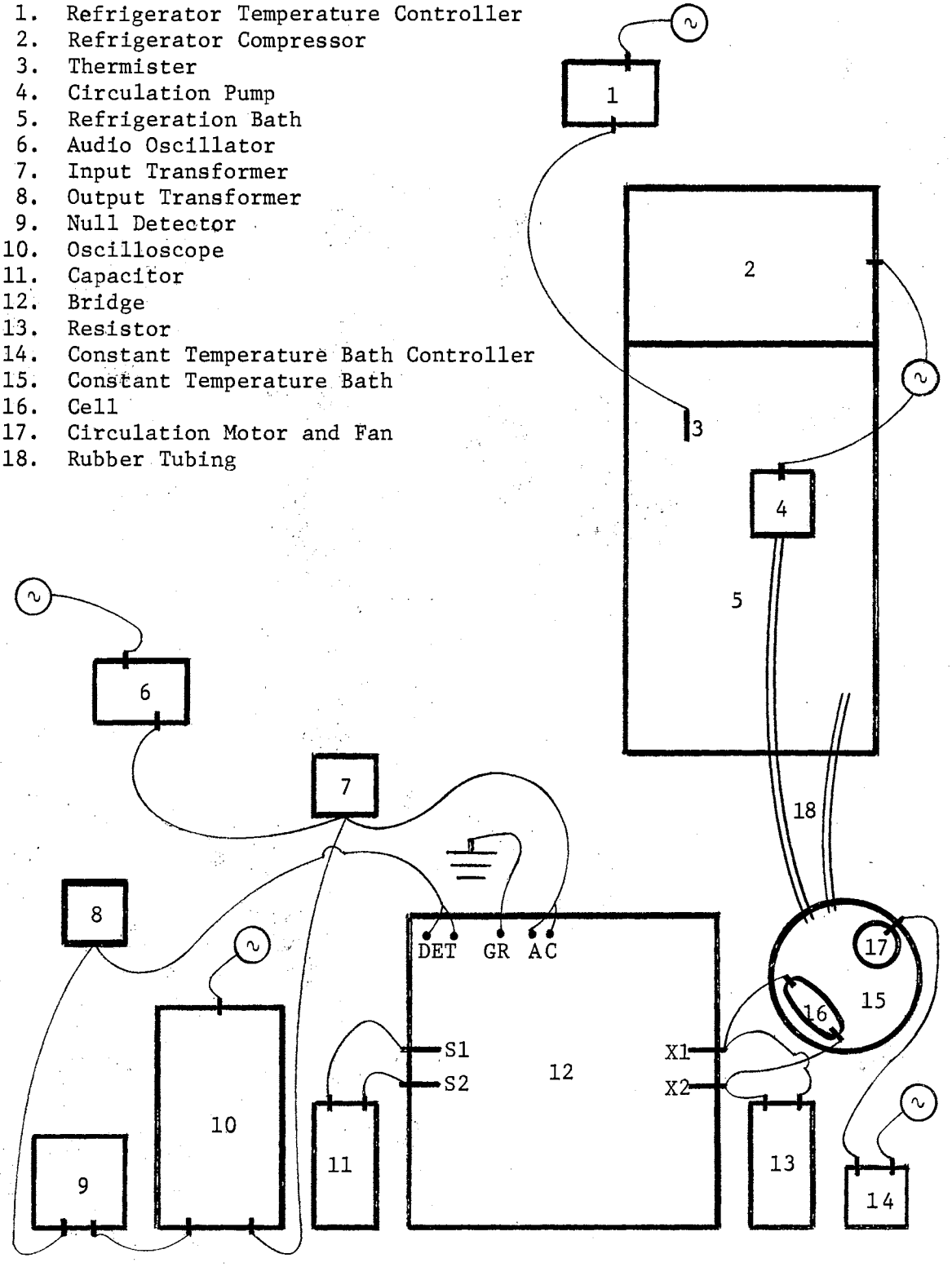


Figure 5. Arrangement of Conductance Apparatus and Constant Temperature System

these effects, the final balancing in a measurement was made with one hand on the dial for the smallest resistance used and the other hand on one of the capacitor dials--no other portion of the body was above the bridge. (3) High resistance measurements (greater than 60 011 Ω) could be accomplished without the use of an external resistance in series with the rheostat arm or in parallel with the unknown resistance. This was done by using one or more of the 10 000-Ω resistors in the bridge as a shunt for the unknown resistance--that is, connecting them across X1 and X2 in Figure 4--and using the remainder in the bridge circuit. The most accurate result was obtained when the resistance of the shunt was near that of the resistance to be measured. The relative precision was better than one part per thousand for those resistances that could be measured directly (less than 60 011 Ω). In view of this, none of the bridge resistors was used as a shunt; rather, an external decade resistor (General Radio Company type 1432-Q) was used. It was set at a nominal value of 60 000 Ω and connected across X1 and X2 in Figure 4; its resistance was measured directly and the unknown resistance was then hooked up in parallel with it across X1 and X2. The resistance box was placed on the table by the bridge. It provided a shunt of the highest resistance that could be directly measured. Other measurements showed that this gave better results for very large resistances than did the use of an external resistor in series with the rheostat arm. Consequently, in this work all resistances in excess of 6×10^4 Ω were measured with the external shunt.

The resistance of a conductor was measured by connecting the conductor across X1 and X2 either with or without a shunt and placing the BR-GR switch in the BR position. (See Figure 4.) All of the components

were turned on and set as described in this section. The gain on the null detector and vertical gain on the oscilloscope were turned to a minimum when these two instruments were turned on. The gain on the null was increased and then resistances on the rheostat were adjusted (starting with the largest) until the needle on the null meter went to a low reading. The gain on the null was further increased along with the vertical gain on the oscilloscope and again the rheostat was adjusted until a minimum signal was obtained. The minimum signal was achieved by alternately balancing the resistance and capacitance in the circuit. Generally, if the resistance in the rheostat was too high the image on the oscilloscope screen would slope in one direction and if it was too low in the other. If the capacitance was either too high or too low the image would form an oval shape. This procedure was repeated--the adjustments becoming more refined--until a balanced circuit was indicated by a horizontal straight line on the oscilloscope screen (and also by a minimum reading on the null detector). Then the BR-GR switch was put in the GR position and slidewire R5 and capacitor C3 (Figure 4) were adjusted to bring the midpoint of the ratio arms to ground potential. Balance was signaled by the current detector in the same way as before. The BR-GR switch was changed to the BR position again and the bridge rebalanced. These steps were repeated until both the bridge and the ground connection were balanced. Under these conditions the resistance being measured, R_x, can be calculated. Equation (4-1) shows that in the absence of a shunt R_x is equal to the sum of all of the resistances in the rheostat arm, R_r. It can be shown that with a shunt,

$$R_x = \frac{R_r R_s}{R_s - R_r}, \qquad (4\text{-}3)$$

in which $\underline{R_S}$ is the resistance of the shunt (189).

Constant Temperature System

A Haake model NBS constant temperature circulator was used as the constant temperature bath for the electrolytic conductance cell. It had a nickel plated copper inner reservoir with a capacity of about 14 dm^3 which was insulated from the outer vessel with glass wool. It had two openings on top--the larger one (about 17 cm in diameter) had a cover consisting of seven concentric rings and a lid, and the smaller one (about 4 cm in diameter) just a lid. The circulation motor (a squirrel cage induction motor with a cooling fan) was housed above the top of the bath. The temperature control consisted of a solid state control box (Haake R22) with a contact thermometer as well as a cooling coil which could be connected to an external refrigeration unit. The relay control box had a dial which governed the heating power between zero and 2000 W by means of the thermoregulator. Another dial allowed up to 80 percent of the heater wattage to be unregulated permanent heat. The thermoregulator (a mercury contact thermometer) had a rotating magnet in a plastic housing mounted on its contact pin. Rotation of the magnet in one direction moved the electrical contact up and in the opposite direction moved it down, thus setting the thermoregulator for a particular temperature.

The constant temperature bath was set on the table adjacent to the bridge (next to $\underline{X1}$ and $\underline{X2}$ in Figure 4) with the control box next to it. Approximately eight dm^3 of paraffin oil (Fisher, N. F., white, light, domestic, Saybolt viscosity 125/135) and four dm^3 of white mineral oil (Purity brand, light) were placed in the reservoir. This oil was used

because of its low dielectric constant--less than five. A 76-mm immersion thermometer (-1 °C to 51 °C and graduated in 1/10-degree) with a Parr thermometer magnifier attached to it was inserted in the bath to be used as a control thermometer. A piece of asbestos board was placed between the control thermometer and the pump housing to shield the thermometer from the heat. A submergible pump (Little Giant 3.2 A-110 V) was placed in a refrigeration bath (water) and its outlet was joined to the inlet of the cooling coil in the oil bath by heavy wall rubber tubing. Heavy wall rubber tubing was attached to the outlet of the cooling coil and returned the water to the refrigeration bath. The refrigeration bath, containing a thermometer, was maintained at 22 °C through the regulation of the refrigerator compressor motor by a model 71 Cole Parmer Thermistemp temperature controller (Yellow Springs Instrument Company). The thermister was put in the refrigeration bath and the controller set at 22 °C. A thermometer was suspended above the bridge to measure the ambient temperature, which was about 23 °C. The control boxes, pumps and compressor were all powered by the 110 V-60 Hz line. The refrigeration bath and compressor were on the floor. The geometrical arrangement of the entire controlled temperature system is shown in Figure 5 along with the conductance bridge assembly.

With this arrangement and following the procedure recommended by the manufacturer for adjusting the thermoregulator it was found that the bath could be maintained at 25.00±0.01 °C when the heat was supplied at about 180 W.

Conductance Cell

The conductance cell employed was a dilution cell which was a modi-

fication of a type of cell designed by Shedlovsky (52) who incorporated the recommendations of Jones and Bollinger (207). The platinum leads to the shiny platinum electrodes were sealed into the cell "behind" the electrodes and the space between the leads outside the cell was filled with thermostat oil rather than the electrolytic solution, thus rendering the stray currents negligible. Electrical contact between the platinum leads and the copper leads to the bridge was made by placing mercury in the glass tubes for the leads. The cell bulb was almost spherical and the electrodes were vertical parallel circular plates separated by a mm or two with their centers aligned on an axis perpendicular to the plane of the plates. The diameter of each electrode was about four cm. The bulb had a glass tube leading from the top, the tube having a stopcock made of Teflon so as to eliminate the need for stopcock grease. (Stopcock grease contamination was a major source of trouble prior to replacing the ground glass stopcock with Teflon.) From the bottom of the cell bulb was another sealed glass tube which led to a 100-cm^3 bulb--the dilution bulb. The dilution bulb had an outer 24/40 standard tapered joint, the top of which was above the top of the cell bulb and was fitted with an inner 24/40 standard tapered stopper. All of the glass in the conductance cell was one piece and was Pyrex. A diagram of the cell is shown in Figure 6.

The cell was filled with a fresh hot solution of 95 percent ethanol saturated with sodium hydroxide. It was emptied a moment later and the process was repeated. The cell was then filled and left standing for 15 minutes, after which it was emptied. De-ionized water from the tap was then run through it for several hours. Fresh cleaning solution was

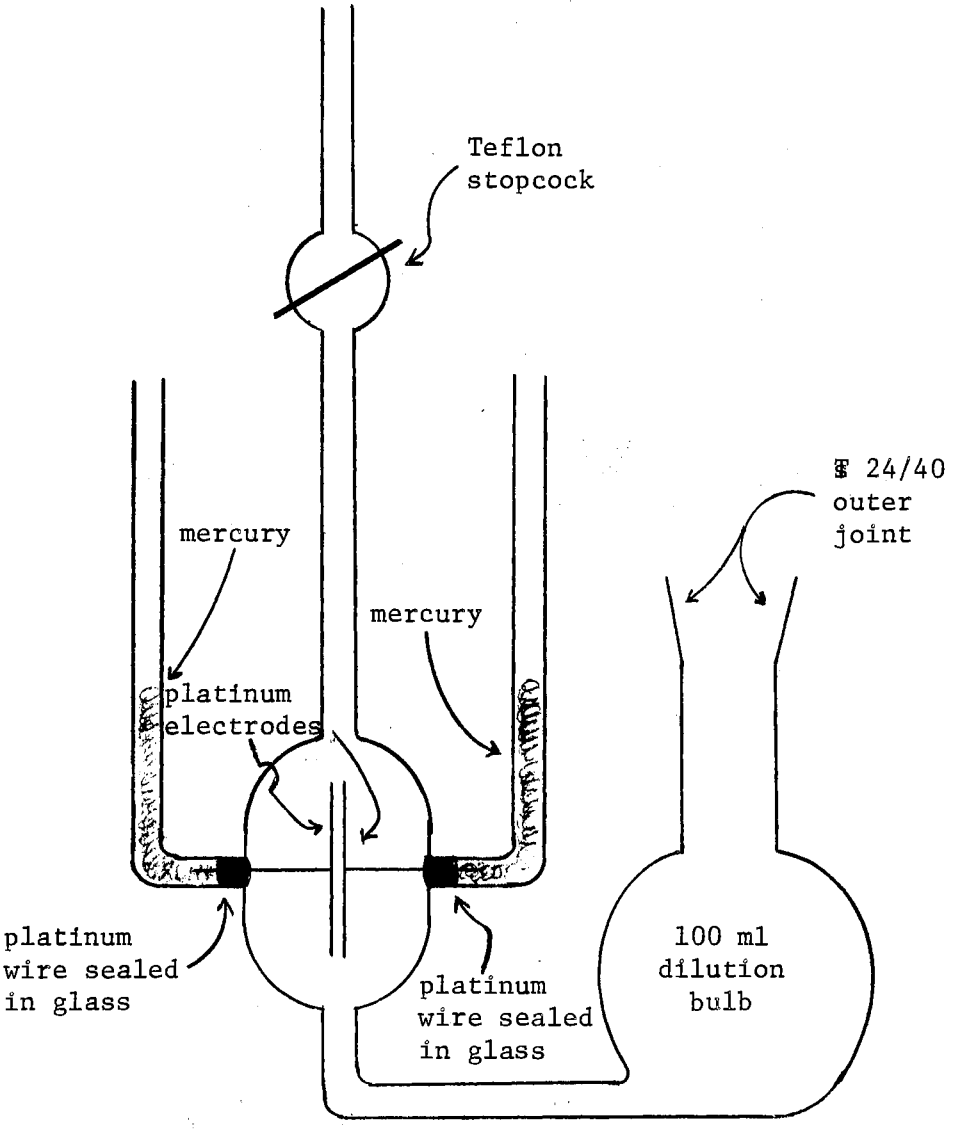


Figure 6. The Conductance Cell

put in the cell and left standing for two hours.[3] The cell was emptied and rinsed three times with de-ionized water; de-ionized water was then run through it overnight. It was rinsed with distilled water three times and stored filled with distilled water. This cleaning procedure was done only once. During the performing of the experiments when the cell was emptied it was always rinsed thoroughly and whenever it was stored it was stored filled with distilled water.

In order to utilize the conductance cell it is necessary to have it calibrated. It is seen from Equation (1-9) that the ratio (ℓ/A) for the conductance cell must be known in order to calculate the specific conductance from the measured resistance. The ratio (ℓ/A) is a fixed quantity for a particular conductance cell and is referred to as the cell constant, J; thus,

$$L_s = \frac{J}{R}. \tag{4-4}$$

The cell constant may be determined by measuring the dimensions of the electrodes and the distance between them or by placing a solution of known specific conductance in the cell and measuring its resistance. Clearly, the former method is entirely unsatisfactory as it is impossible to make these measurements with sufficient accuracy; in addition, the cell constant includes other environmental characteristics peculiar to the cell. The latter method has been done in two ways. One makes use of a conductance equation to calculate the equivalent conductance of the reference solution of known concentration. The specific conductance

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[3]The cleaning solution was prepared by adding 375 cm^3 of concentrated nitric acid to a solution of 10 g of potassium dichromate in 100 cm^3 of water.

is then calculated from Equation (1-2), the resistance is measured in the conductance cell, and the cell constant calculated from Equation (4-4). This method has been used by Lind, Zwolenik and Fuoss (124) and has the advantage of not requiring a solution of a specified concentration or even a particular temperature. It was not used in this work because it was desired to have the calibration of the cell independent of the theory under investigation. The other way requires a conductance solution of a particular concentration and a designated temperature for which its specific conductance is known; its resistance is measured and the cell constant calculated from Equation (4-4). This is the method employed in this work.

Kohlrausch (209) used aqueous potassium chloride solutions of various concentrations as standard reference solutions. Parker and Parker (210) obtained different values for the specific conductance of aqueous potassium chloride solutions. Because of this discrepancy Jones and Bradshaw (211) undertook an extensive and very precise investigation of the specific conductance of aqueous potassium chloride solutions and their values are considered to be the most reliable available. Their measurements were made in several cells and mercury was used as the reference substance. They obtained specific conductance measurements for three standard potassium chloride solutions at different concentrations at 0 °C, 18 °C and 25 °C. The concentrations were 1, 0.1 and 0.01 demal solutions.[4] Jones and Bradshaw (211) defined a one hundredth

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[4]Parker and Parker (210) suggested the term demal; a one demal solution is one containing one gram equivalent weight of salt per cubic decimeter of solution and the letter D is used to denote demality. At that time the liter was defined in such a manner that it was not identical to the cubic decimeter; with the present definition of a liter this definition for demal is tantamount to the definition of normal.

demal potassium chloride solution as one containing 0.745263 g of potassium chloride per kg of solution; they found its specific conductance, $\underline{L_{s(KCl)}}$, to be $1.40877 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$ at 25.000±0.001 °C.

A 0.01000 D KCl solution was prepared by measuring 0.7452 g of potassium chloride on a tared weighing paper with a single pan substitution balance (Mettler type B5H26). The potassium chloride was transferred quantitatively to a screw capped polyethylene bottle which had been tared on a solution balance. Distilled water was added to the bottle on the pan of the solution balance; weights, which had been calibrated by measuring their mass on the single pan substitution balance used for the potassium chloride, were added during this time to give an approximation of the mass. The final water was added in very small increments. The mass of the solution, obtained by difference, was 1000.14±0.02 g. The standard solution was kept capped in this bottle.

The conductance cell was rinsed with and then filled with distilled water which had been taken from the same batch used for the preparation of the standard potassium chloride solution. The cell was placed in the constant temperature bath at 25.00±0.01 °C and connected to the conductance bridge. The resistance of the water, $\underline{R_{H_2O}}$, was measured and found to be $(1.40\pm0.02) \times 10^4\ \Omega$. The cell was disconnected, removed, rinsed three times with distilled water, then three times with the standard solution, filled with the standard solution, placed in the constant temperature bath at 25.00±0.01 °C and connected to the conductance bridge. The external capacitor, which was not used for the distilled water determination, was connected to the bridge and it was found necessary to increase the capacitance even more; this was accomplished by connecting a one μF capacitor in parallel with the decade capacitor.

Five measurements of the solution resistance were made, the cell was removed, the contents mixed between the two bulbs, the cell replaced and five more resistance measurements made. The procedure described in the preceding sentence was repeated with another portion of the standard solution. The average value of the resistance for the two samples of the standard solution, R_{soln}, was 12.3138±0.0050 Ω.

An uncorrected cell constant, J', was calculated from Equation (4-4):

$$J' = L_{s(KCl)}R_{soln} = 0.017347 \text{ cm}^{-1}. \quad (4\text{-}5)$$

The uncorrected cell constant was used to calculate the specific conductance of the water, $L_{s(H_2O)}$:

$$L_{s(H_2O)} = \frac{J'}{R_{H_2O}} = 1.24 \times 10^{-6} \ \Omega^{-1} \text{ cm}^{-1}. \quad (4\text{-}6)$$

(Jones and Bradshaw (211) used water with a specific conductance of 1.0×10^{-6} Ω^{-1} cm^{-1} more or less at 25 °C in the preparation of their standard solutions.) The corrected cell constant, J, was obtained by making use of the fact that specific conductances are additive:

$$J = (L_{s(KCl)} + L_{s(H_2O)})R_{soln} = 0.0173626 \text{ cm}^{-1}. \quad (4\text{-}7)$$

If the deviation in the measured resistance for the standard solution is taken into account a value of 0.017363±0.000007 cm^{-1} is obtained for the cell constant. This reflects the error due to the measurement of the resistance including the temperature fluctuations. It does not include an estimate of the error due to the preparation of the standard solution; hence, it gives a measure of the precision expected for a given solution of 0.01 D KCl with the apparatus and procedure used.

One way of using a dilution cell is to start with a concentrated solution and add solvent in increments, thus obtaining a more dilute

solution with each portion added. Another means is to use a dilute solution initially and add increments of solute and obtain a more concentrated solution each time. The latter method was chosen in this work because it offers several advantages. It allows for a much broader range of concentrations to be used without the necessity of emptying the cell. Furthermore, if complete mixing has not occurred the relative error is much smaller when the solution being replaced is more dilute than it is when the replaced solution is more concentrated.

Dry Box

The basic material for the dry box was a commercially built (Manostat) dry box constructed of Plexiglass. Plexiglass is not a desirable building material for use with acetone solutions, but it was available and did work--fortunately, acetone was never spilled in it. The box was modified considerably to meet the needs of this work. In its final form the main chamber was about one meter wide, 60 cm high and 60 cm from front to back. The front face sloped back from bottom to top and contained two 20-cm (diameter) holes fitted with long sleeved rubber gloves for use inside the chamber. The centers of these holes were about 50 cm from each other and 20 cm from the bottom. A Plexiglass shelf was built in the back and a single pan substitution analytical balance (Mettler type H-5) with a capacity of 160 g was placed on it. A double 110 V electrical receptacle was mounted on the outside of the back of the dry box. Holes were cut in the dry box so that only the two polarized outlets were inside the box. The box also contained a sealed-in copper wire which served to ground the balance pan in order to reduce the static electricity. All connections and seams were sealed with a

caulking material (Silicone Seal). The left end of the box contained a circular hole with a diameter of about 30 cm. Extending out horizontally from this hole was a Plexiglass cylinder of the same diameter as the hole and about 35 cm long. This cylinder had a Plexiglass door on each end and served as the entry compartment. The door between the entry compartment and the chamber could be opened only from the chamber and the other door could be opened only from outside the system. The outside door was held closed with clamps except when an item was being transferred into or out of the system. The entry compartment contained a plate supported on its bottom which provided a level area about 20 cm wide and the length of the cylinder. A hole on the right side of the chamber and another in the back of the entry compartment served as inlets for nitrogen. These had copper tubing connected to them from the outside. (The Plexiglass was machine threaded.) Each tube had a valve and beyond the valves the tubes were united by a "T" joint. The other branch of the "T" joint led to the nitrogen source. The nitrogen was supplied from a cylinder and the flow controlled by a nitrogen regulator (Purox CGA-580); it passed through a battery of tubes and flasks containing molecular sieves and indicating silica gel before entering the "T." The valves were used to control the relative amounts of nitrogen going through the chamber and entry compartment. On the left side of the chamber and on the back side of the entry compartment were the nitrogen exit holes for the chamber and entry compartments, respectively; these were machine fitted with copper tubing from the outside. Each copper tube was joined to rubber tubing which in turn was attached to the side arm of a 250-cm^3 Pyrex filtering flask. Each filtering flask had a fitted rubber stopper with a piece of glass tubing inserted in it.

This glass tube was connected by rubber tubing to another glass tube which was suspended in a 125-cm^3 Pyrex Erlenmeyer flask. The Erlenmeyer flask contained paraffin oil (Fisher, N.F., white, light, domestic, Saybolt viscosity 125/135) and the glass tubing was immersed about one cm in the oil. The filtering flask was simply a trap to prevent oil from backing into the box. The oil in the Erlenmeyer flask, however, served several purposes: (1) It prevented the system from being exposed to the atmosphere. (2) It functioned qualitatively as a flow meter--the regulator was adjusted so that a small constant amount of nitrogen bubbled through the oil. (3) It kept a positive pressure (relative to the atmosphere) in the dry box which could be adjusted by vertical movement of the tubing in the oil.

Five metal pans which were about 20 cm long, 10 cm wide and six cm deep were cleaned, dried, half filled with molecular sieves containing indicating silica gel, and quickly transferred into the entry compartment. One was retained in the entry compartment and the other four were put inside the chamber. These desiccants were kept there throughout the work.

Originally, static electricity in the box was a major problem--one which made it impossible to make a quantitative transfer of lithium bromide on the balance. The Plexiglass appeared to amplify the effects which are normally associated with a dry atmosphere. This problem was solved by placing several "Nuclear" sealed radioactive sources (radium) in the chamber--two of the disks were put in the balance case.

Maintenance on the box was negligible. When the box was not in use it was flushed with nitrogen every few days. Occasionally the desiccant in the box was removed, regenerated by heating in an oven at 400 °C for

several hours and returned to the box.

Each item was dried before being transferred into the box. The outside door was opened only as long as was necessary for the item to be placed in the entry compartment and never when the door into the chamber was open nor when nitrogen was not flowing through the chamber. An item was left in the entry compartment for a minimum of 15 minutes with the nitrogen flowing. Then the chamber door was opened and the item passed into the chamber. Nitrogen was passed through the chamber during all operations. The only restriction for transferring an item out of the chamber was that the chamber door not be opened unless the outside door had been closed for at least 15 minutes. Once an item had been put in the entry compartment and the chamber door closed, the outside door could be opened immediately and the item removed.

As a practical matter it was sometimes difficult to record masses in a series of measurements being made with the balance in the dry box. In some instances this problem was overcome by reading the masses into a tape recorder and later transcribing them into the laboratory notebook.

CHAPTER V

TECHNIQUES EMPLOYED FOR PROCUREMENT OF DATA

It is manifest from Equation (2-1) that it is necessary to determine the concentration, resistance, dielectric constant, viscosity and temperature of the system. These data were acquired for five different solvent systems. A series of measurements, in which the normality of lithium bromide was varied from about 10^{-5} eq dm^{-3} to 10^{-3} eq dm^{-3}, was made on each solvent system. The solvents used were acetone, 0.02063 molal bromosuccinic acid in acetone, 0.05009 molal bromosuccinic acid in acetone, 0.09958 molal bromosuccinic acid in acetone and 0.05047 molal dimethyl bromosuccinate in acetone and are designated as Solvent I, Solvent II, Solvent III, Solvent IV and Solvent V, respectively.

The mixed solvents--Solvents II, III, IV and V--were prepared in the dry box by transferring a roughly calculated quantity of the acid or ester from its storage container to a tared 16-oz polyethylene bottle.[1] A syringe was used for the ester. The mass of the bottle plus acid or ester was measured and the mass of the acid or ester found by

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[1]All of the polyethylene bottles used for solvents and solutions had plastic screw caps fitted with polyethylene cone liners and were tested to ascertain that there was no solvent leakage. A felt tipped pen was used to mark them with identifying symbols and 25-cm^3 graduation lines. The bottles were washed with soap and water and rinsed with de-ionized water, distilled water and acetone. They were dried by passing dry nitrogen (using the same assembly as was used for flushing the distillation column) through them.

difference. About 500 cm^3 of acetone was added and the tared screw cap put on the bottle. The contents were thoroughly mixed. The bottle was removed from the dry box and its mass measured on the solution balance which was used in the preparation of the standard potassium chloride solution. The mass of the acetone was computed by difference. The bottle was returned to the dry box and kept there until the particular series of measurements was completed. The molality of the acid or ester was calculated. After each solvent was made, its infrared spectrum was obtained and none showed an absorption band at 3600 cm^{-1}.

Concentration

For each solvent a solution of about 0.2 molal lithium bromide was prepared in the dry box by transferring approximately two g of the salt to a tared eight-oz polyethylene bottle. The mass of the bottle plus salt was measured, about 125 cm^3 of the solvent added and the mass remeasured. The mass of the lithium bromide and of the solvent were determined by difference. Both the molality of the lithium bromide and the number of grams of lithium bromide per gram of solution were calculated. This solution, which was thoroughly mixed, was designated as the concentrated stock solution. A sample of the solution was withdrawn from the bottle and its infrared spectrum obtained; there was no absorption peak at 3600 cm^{-1}.

Approximately five cm^3 of the concentrated stock solution was tra quantitatively transferred to a four-oz polyethylene bottle. The transfer was made with a weighing buret (10-cm^3) and the mass of the solution determined by the difference in mass of the weighing buret. The

mass of the bottle plus solution was measured, about 100 cm^3 of solvent was added, the mass remeasured and the contents fully mixed. Again, the molality of the lithium bromide and the number of grams of lithium bromide per gram of solution were calculated. This solution was referred to as the intermediate stock solution. A dilute stock solution was prepared in the same manner as the intermediate stock solution from about eight cm^3 of the intermediate stock solution and 85-90 cm^3 of the solvent. The intermediate and dilute stock solutions were 10^{-2} molal and 10^{-3} molal, respectively, in lithium bromide.

Prior to a series of measurements the conductance cell, with the Teflon stopcock removed, was dried in an oven at 110 °C. Upon removal from the oven a minimal amount of Apiezon T grease was put on the ground glass stopper. The cell was put in the dry box. It was not opened outside the dry box during the series of measurements and was never kept open longer than necessary. About 60 cm^3 of solvent was transferred quantitatively from an eight-oz polyethylene bottle to the cell by pouring it into the dilution bulb; this was the minimum amount required to fill the cell bulb. The mass of the solvent added was found from the difference in the mass of the solvent bottle. The cell was removed from the dry box, the resistance of the solution was measured on the bridge and the cell was returned to the dry box.

Dilute stock solution was added to the solution in the cell by means of the weighing buret. An adapter, with an inner 24/40 standard tapered joint and outer ground glass joint of the same size as the inner ground glass joint on the buret, was placed in the 24/40 standard tapered joint of the dilution bulb. The buret was secured in the adapter and some of the stock solution was dripped into the solution in the

dilution bulb without first coming in contact with any parts of the cell. The weighing buret was then returned to its support and the mass of the stock solution added obtained by difference. The contents of the cell were mixed by careful tilting of the cell and manipulation of the stopcock and stopper. The solution was passed back and forth several times making certain that it never reached the stopcock nor came in contact with the stopper. Finally the cell bulb was filled slowly to insure the absence of bubbles. The solution was run into the tube on top of the bulb to a height of about one cm above the bulb and the stopcock was closed. The pressure was adjusted to atmospheric pressure by alternately opening and closing the stopper and stopcock. After the cell was removed from the dry box, the resistance of the solution was measured and the cell was returned to the dry box.

The procedure just described was repeated several times with the dilute stock solution and then with the intermediate stock solution. About ten concentrations with a hundredfold range were obtained. A portion of the final solution in the cell (the most concentrated solution) was removed and the infrared spectrum taken; no absorption band was observed at 3600 cm^{-1}.

The normality of the solute is required for the calculation of the equivalent conductance and in the conductance equation. Inasmuch as the conductance solutions were prepared by mass measurement it was necessary to obtain their densities in order to determine the normal concentration of lithium bromide. In all cases the density of the solution was assumed to be the same as the density of the solvent. This approximation is easily justified for solutions as dilute as the ones used. For example, Mahan (166) found the density of 1×10^{-3} molal lithium

bromide in acetone, which is comparable to the most concentrated solutions used in this work, to be greater than that of the acetone used in the preparation of his solution by only 2 x 10^{-4} g cm^{-3}. The density of the acetone was taken from the literature for this work: 0.7845 g cm^{-3} (179). The densities of the acetone-bromosuccinic acid mixed solvents were calculated from data obtained by Muller (165). He found that the density of a solution, δ, of c_m molal bromosuccinic acid in acetone is given by the expression

$$\delta = \delta_o(1 + 0.129c_m), \qquad (5\text{-}1)$$

in which δ_o is the density of acetone. Equation (5-1) yields densities of 0.7866 g cm^{-3}, 0.7896 g cm^{-3} and 0.7946 g cm^{-3} for Solvents II, III and IV, respectively. The density of the acetone-dimethyl bromosuccinate mixed solvent was estimated by assuming the density of mixtures of the two compounds to be linear functions of their mole fractions. Beilstein (212) lists the density of dimethyl bromosuccinate as 1.5094 g cm^{-3} at 15 °C. If the density is taken as 1.5 g cm^{-3} for dimethyl bromosuccinate, a value of 0.7866 g cm^{-3} is obtained for Solvent V. This appears to be a somewhat arbitrary way for determining the density, but it should yield a value close to the correct value. Since only one solvent system of acetone and dimethyl bromosuccinate was used and since it is the changes in concentration which are critical in evaluating the parameters of the conductance equation, the density of the solvent, which is a constant, does not have an appreciable effect on the final outcome.

With these data it is possible to calculate the normality of the lithium bromide for each solution prepared. A computer program was written to calculate the molality and normality of each solution in a

series. The input required for the program was the number of grams of solvent originally in the cell, the formula mass of the solute, the density of the solvent (in g cm^{-3}), the number of grams of solute per gram of solution for each of the three stock solutions, the number of measurements made in the series and the number of grams of stock solution added in each increment along with the identity of the stock solution. The computer program is given in Appendix C.

Resistance

Kohlrausch's method (the adaptation of the Wheatstone bridge for the determination of electrolytic conductance) was used for measuring the resistance of all of the solvents and solutions. The conductance cell (shown in Figure 6) containing the electrolytic solution had to be manipulated carefully in order to get it into the constant temperature bath without allowing bubbles to pass from the dilution bulb into the cell bulb. If bubbles did pass into the cell bulb the liquid level dropped so that the geometry of the solution with respect to the electrodes was changed; in this event the cell was put in the dry box for readjustment of the solution and then returned to the constant temperature bath. The cell was supported in the bath by an extension clamp with asbestos sleeves. The extension clamp was attached by a clamp holder to a vertical support which was part of the bath. The clamp was held so that the level of the bath oil was just below the top of the ground glass joint on the dilution bulb.

Electrical contact between the cell and the bridge was made with copper wire (B & S gauge no. 12). An end of one wire was fastened to the terminal at X2 on the bridge (Figure 4) and the other end immersed

in the mercury in the cell electrode lead tube on the side toward the dilution bulb. The other wire was connected in a similar fashion from X1 to the other lead tube of the cell. The length of the wire between each lead tube and the bridge terminal was about 25 cm. The wires were separated from each other by about ten cm in order to reduce the capacitance effect between them. Time was allowed for the attainment of thermal equilibrium; then a minimum of three resistance measurements was made at five minute intervals and the average value calculated. The external resistor was not used with Solvents II, III and IV or any of the lithium bromide solutions, but was required for the determination of the specific conductance of Solvents I and V. The external capacitor was not required for the solvents or dilute lithium bromide solutions, but was for all of the more concentrated lithium bromide solutions. Upon completion of the measurements the gain on the null detector and the vertical gain on the oscilloscope were set at a minimum and the cell disconnected from the bridge. The cell was removed from the bath and the oil wiped from it with a cloth towel. The cell was then returned to the dry box.

Dielectric Constant

The dielectric constant of a medium is the ratio of the capacitance of a capacitor filled with the medium to the capacitance of the empty capacitor. The dielectric constant of a vacuum is defined to be unity and that of air at one atmosphere is given in the literature as 1.00059 (189). A number of methods has been developed for experimentally determining the dielectric constant of a medium. Most of the methods yield inaccurate results for liquids which are appreciably conducting.

(Debye's (213) Polar Molecules is a classic discussion of the theories of dielectrics.)

Muller (165) used a capacitance measuring assembly (General Radio Company type 716-C capacitance bridge with a type 716-P4 guard circuit) and a dielectric cell, similar to the one described by Sadek and Fuoss (214), in a vain endeavor to measure the dielectric constant of solutions of bromosuccinic acid in acetone. He did succeed, however, in determining the dielectric constant at 25 °C of acetone and solutions of succinic acid (0.01, 0.05 and 0.1 molal) in acetone and found them to be essentially the same. Each of the three solutions had a dielectric constant which was greater than that of the acetone by 0.2. He suggested that the nonsuccess with bromosuccinic acid solutions was due to a high loss factor. The literature values for the dissociation constants of succinic acid and bromosuccinic acid are 6.89×10^{-5} and 2.78×10^{-3}, respectively, for aqueous solutions at 25 °C (171) (212). Brown (215) attempted and failed to measure the dielectric constant of 1-butanol with a similar apparatus and attributed his inability to obtain results to the high conductance of 1-butanol. The literature lists the dielectric constant and specific conductance of 1-butanol at 25 °C as 17.1 and 9.12×10^{-9} Ω^{-1} cm^{-1}, respectively (179).

Since this was the only dielectric constant equipment available and in view of Muller's (165) results, it was decided to use the literature value for the dielectric constant of acetone as the dielectric constant for each of the solvents utilized in this work. This value is 20.7 (179).

Viscosity

Viscosity is the force required to produce a unit rate of shear between two layers in a fluid which are separated by a unit distance. Poiseuille (216) discovered that the viscosity of water is increased by the addition of some salts and decreased by others. Arrhenius (217) found the viscosity of dilute solutions to be a linear function of the concentration of the solute. However, accurate measurements of viscosity made by Grüneisen (218) (219) demonstrated that the viscosity of an electrolytic solution is not a linear function of concentration for dilute solutions and that the deviation from linearity increases with concentration. This deviation--the Grüneisen effect--does not occur in solutions of nonelectrolytes. Jones and coworkers (220) (221) showed experimentally that the relative viscosity, η_{rel}, of an electrolytic solution is a linear function of the square root of the concentration of the electrolyte and can be delineated by the equation

$$\eta_{rel} = 1 + M_1\sqrt{c} + M_2 c, \tag{5-2}$$

in which M_1 and M_2 are adjustable parameters.[2] This semiempirical equation is termed the Jones-Dole equation. The coefficient M_1 (which is a positive quantity) represents the contribution to the viscosity from the ion-ion interaction and has been identified as the slope, M_3, of the

---

[2]The relative viscosity of a solution is defined by the equation

$$\eta_{rel} = \frac{\eta'}{\eta}, \tag{5-3}$$

in which η' is the viscosity of the solution and η is the viscosity of the pure solvent at the same temperature. It is a measure of the change in viscosity of a fluid (solvent) due to the addition of some substance (solute).

theoretical limiting law of Falkenhagen (222) (223) (224) (225) which takes the form

$$\eta_{rel} = 1 + M_3\sqrt{c}, \tag{5-4}$$

where M_3 can be calculated from properties of the system. The coefficient M_2 (which may be positive or negative) has been interpreted in terms of ion-solvent interaction; it is highly specific and is an approximately additive property of the ions (130). Equation (5-2) can be rearranged to give

$$\frac{\eta_{rel} - 1}{\sqrt{c}} = M_1 + M_2\sqrt{c}. \tag{5-5}$$

The experimental values of M_1 and M_2 are then determined by fitting a linear curve to a plot of $(\eta_{rel} - 1)/\sqrt{c}$ versus $\sqrt{c}$; the slope corresponds to M_2 and the intercept to M_1. It should be pointed out that other viscosity equations have been developed, but were not utilized in this work (37).

The value used for the viscosity of acetone was obtained from the literature: 3.02×10^{-3} P (179). The viscosities of the acetone-bromosuccinic acid mixed solvents were derived from data acquired by Muller (165) who made viscosity measurements with a special type of viscometer (which has been described by Tuan and Fuoss (226)) on solutions of varying amounts of bromosuccinic acid in acetone. He plotted the left side of Equation (5-5) against the square root of the concentration and obtained values of 0.0150 and 0.4137 for M_1 and M_2, respectively. These values of M_1 and M_2 were substituted into Equation (5-2) and subsequently the viscosities were calculated from Equations (5-2) and (5-3); the outcome was 3.05×10^{-3} P, 3.08×10^{-3} P and 3.13×10^{-3} P for Solvents II, III and IV, respectively. Perusal of viscosity data

available for nonelectrolytic solutions indicates that the viscosity of a solution of an ester in acetone at the concentration of the acetone-dimethyl bromosuccinate mixed solvent would not be appreciably different from the viscosity of the pure acetone. In view of this, coupled with the facts that the viscosity of acetone is known to just three significant figures and that only one solvent system of acetone and dimethyl bromosuccinate was used, the viscosity of Solvent V was considered to be identical to that of acetone: 3.02×10^{-3} P.

Temperature

All resistance measurements were made in the constant temperature bath which was maintained at 25.00±0.01 °C. Before any measurements were made on a solution it was left in the bath for a minimum of 15 minutes to allow thermal equilibrium to be established. The ambient temperature was about 23 °C.

CHAPTER VI

THE RESULTS

Compilation of Data

Each set of measurements with a particular solvent system is referred to as a series and designated by a Roman numeral--the same Roman numeral as used for the identification of the solvent. Within each series the measured concentration and corresponding data are referred to as a point and each point in a series is represented by the Roman numeral for the series followed by an Arabic numeral. The Arabic numeral "1" is used for the pure solvent, the numeral "2" for the most dilute lithium bromide solution with that solvent, "3" for the next most dilute, etc. For example, "Point IV2" denotes the most dilute solution of lithium bromide in 0.09958 molal bromosuccinic acid in acetone.

The results which are given in this section include only those particulars which are experimentally measured or evaluated from a definition and do not require any theory of conductance for their calculation. Such items are the cell constant, dielectric constant, temperature, viscosity, density, resistance, concentration (calculated with the computer program given in Appendix C), specific conductance (calculated from Equation (4-4)) and equivalent conductance (calculated from Equation (1-2)). These are summarized for each series in Tables III through VII. In these tables both the uncorrected and corrected specific conductances

TABLE III

SERIES I: LITHIUM BROMIDE IN ACETONE

Point	$c_m \times 10^5$ $\left(\frac{\text{mol (solute)}}{\text{kg (solvent)}}\right)$	$c_n \times 10^5$ $\left(\frac{\text{eq (solute)}}{\text{dm}^3\text{ (solution)}}\right)$	R (Ω)	$L_s \times 10^6$ (Ω^{-1} cm^{-1}) (uncorrected)	$L_s \times 10^6$ (Ω^{-1} cm^{-1}) (corrected)	Λ $\left(\frac{\text{cm}^2}{\Omega\text{ eq}}\right)$
I1			951 300	.01825		
I2	1.609	1.262	7300.5±3.1	2.378	2.360	187.0
I3	3.378	2.650	3618.35±0.17	4.799	4.780	180.4
I4	6.578	5.160	1971.76±0.14	8.806	8.788	170.3
I5	11.02	8.644	1264.443±0.040	13.73	13.71	158.6
I6	17.08	13.40	884.037±0.032	19.64	19.62	146.4
I7	24.94	19.56	658.359±0.009	26.37	26.36	134.7
I8	39.29	30.83	470.482±0.004	36.90	36.89	119.6
I9	68.62	53.84	317.354±0.001	54.71	54.69	101.6
I10	118.5	92.96	220.425±0.002	78.77	78.75	84.72

Cell constant: 0.017363 cm^{-1}
Temperature: 25.00 °C
Viscosity: 3.02 x 10^{-3} P

Density: 0.7845 g cm^{-3}
Dielectric constant: 20.7
Specific conductance of acetone: 1.825 x 10^{-8} Ω^{-1} cm^{-1}

TABLE IV

SERIES II: LITHIUM BROMIDE IN 0.02063 MOLAL BROMOSUCCINIC ACID IN ACETONE

Point	$c_m \times 10^5$ $\left(\frac{\text{mol (solute)}}{\text{kg (solvent)}}\right)$	$c_n \times 10^5$ $\left(\frac{\text{eq (solute)}}{\text{dm}^3\text{ (solution)}}\right)$	R (Ω)	$L_s \times 10^6$ (Ω^{-1} cm^{-1}) (uncorrected)	$L_s \times 10^6$ (Ω^{-1} cm^{-1}) (corrected)	Λ $\left(\frac{\text{cm}^2}{\Omega\text{ eq}}\right)$
II1			22 546±3	.7701		
II2	.9544	.7508	8993.1±1.6	1.931	1.161	154.6
II3	1.867	1.469	5639.6±0.2	3.079	2.309	157.2
II4	4.740	3.729	2660.46±0.08	6.526	5.756	154.4
II5	7.344	5.777	1830.70±0.08	9.484	8.714	150.8
II6	10.97	8.633	1295.89±0.05	13.40	12.63	146.3
II7	14.32	11.26	1032.55±0.05	16.82	16.04	142.5
II8	28.68	22.56	584.50±0.02	29.71	28.94	128.3
II9	43.39	34.13	421.058±0.008	41.24	40.47	118.6
II10	70.58	55.52	290.862±0.002	59.69	58.92	106.1
II11	123.3	96.95	194.720±0.006	89.17	88.40	91.18

Cell constant: 0.017363 cm^{-1} Density: 0.7866 g cm^{-3}

Temperature: 25.00 °C Dielectric constant: 20.7

Viscosity: 3.05 x 10^{-3} P Specific conductance of acetone: 2.177 x 10^{-8} Ω^{-1} cm^{-1}

TABLE V

SERIES III: LITHIUM BROMIDE IN 0.05009 MOLAL BROMOSUCCINIC ACID IN ACETONE

Point	$c_m \times 10^5$ $\left(\frac{\text{mol (solute)}}{\text{kg (solvent)}}\right)$	$c_n \times 10^5$ $\left(\frac{\text{eq (solute)}}{\text{dm}^3\text{ (solution)}}\right)$	R (Ω)	$L_s \times 10^6$ (Ω^{-1} cm^{-1}) (uncorrected)	$L_s \times 10^6$ (Ω^{-1} cm^{-1}) (corrected)	Λ $\left(\frac{\text{cm}^2}{\Omega\text{ eq}}\right)$
III1			12 328.7±1.7	1.408		
III2	.7629	.6024	7693.4±0.6	2.257	0.849	140.9
III3	1.537	1.214	5603.6±0.2	3.099	1.690	139.3
III4	4.247	3.354	2884.32±0.13	6.020	4.612	137.5
III5	6.896	5.445	1974.38±0.04	8.794	7.386	135.7
III6	10.44	8.243	1401.71±0.01	12.39	10.98	133.2
III7	13.78	10.88	1108.97±0.04	15.66	14.25	131.0
III8	28.60	22.59	601.42±0.02	28.87	27.46	121.6
III9	45.65	36.04	408.088±0.007	42.55	41.14	114.1
III10	75.09	59.29	274.549±0.006	63.24	61.83	104.3
III11	127.0	100.2	183.970±0.007	94.38	92.97	92.79

Cell constant: 0.017363 cm^{-1}
Temperature: 25.00 °C
Viscosity: 3.08 x 10^{-3} P
Density: 0.7896 g cm^{-3}
Dielectric constant: 20.7
Specific conductance of acetone: 1.691 x 10^{-8} Ω^{-1} cm^{-1}

TABLE VI

SERIES IV: LITHIUM BROMIDE IN 0.09958 MOLAL BROMOSUCCINIC ACID IN ACETONE

Point	$c_m \times 10^5$ $\left(\frac{\text{mol (solute)}}{\text{kg (solvent)}}\right)$	$c_n \times 10^5$ $\left(\frac{\text{eq (solute)}}{\text{dm}^3\text{ (solution)}}\right)$	R (Ω)	$L_s \times 10^6$ (Ω^{-1} cm^{-1}) (uncorrected)	$L_s \times 10^6$ (Ω^{-1} cm^{-1}) (corrected)	Λ $\left(\frac{\text{cm}^2}{\Omega\text{ eq}}\right)$
IV1			6703.2±0.2	2.590		
IV2	.8724	.6932	4953.5±0.1	3.505	0.915	132.0
IV3	1.678	1.333	3976.3±0.2	4.367	1.777	133.3
IV4	3.352	2.663	2856.9±0.1	6.078	3.488	131.0
IV5	6.330	5.030	1896.22±0.27	9.157	6.567	130.5
IV6	10.22	8.122	1330.00±0.06	13.05	10.46	128.8
IV7	13.80	10.97	1048.32±0.04	16.56	13.97	127.4
IV8	29.80	23.68	560.480±0.026	30.98	28.39	119.9
IV9	47.23	37.53	384.762±0.010	45.13	42.54	113.3
IV10	77.07	61.24	257.689±0.001	67.38	64.79	105.8
IV11	133.1	105.8	167.755±0.004	103.5	100.9	95.38

Cell constant: 0.017363 cm^{-1}
Temperature: 25.00 °C
Viscosity: 3.13 x 10^{-3} P

Density: 0.7946 g cm^{-3}
Dielectric constant: 20.7
Specific conductance of acetone: 2.064 x 10^{-8} Ω^{-1} cm^{-1}

TABLE VII

SERIES V: LITHIUM BROMIDE IN 0.05047 MOLAL DIMETHYL BROMOSUCCINATE IN ACETONE

Point	$c_m \times 10^5$ $\left(\frac{\text{mol (solute)}}{\text{kg (solvent)}}\right)$	$c_n \times 10^6$ $\left(\frac{\text{eq (solute)}}{\text{dm}^3\text{ (solution)}}\right)$	R (Ω)	$L_s \times 10^6$ (Ω^{-1} cm^{-1}) (uncorrected)	$L_s \times 10^6$ (Ω^{-1} cm^{-1}) (corrected)	Λ $\left(\frac{\text{cm}^2}{\Omega\text{ eq}}\right)$
V1			90 860	.1911		
V2	1.245	.9796	9267±3	1.874	1.682	171.8
V3	2.088	1.642	5768.8±4.4	3.010	2.819	171.7
V4	3.271	2.573	3787.9±1.0	4.584	4.393	170.7
V5	5.282	4.155	2440.3±0.4	7.115	6.924	166.6
V6	8.326	6.549	1631.6±0.1	10.64	10.45	159.6
*V7	11.7-	9.2--	1196.61±0.04	14.5-	14.3-	156.-
V8	49.6-	39.0-	396.78±0.01	43.8-	43.6-	111.7
V9	84.4-	66.4-	273.10±0.02	63.6-	63.4-	95.5-

Cell constant: 0.017363 cm^{-1} Density: 0.7866 g cm^{-3}
Temperature: 25.00 °C Dielectric constant: 20.7
Viscosity: 3.02 x 10^{-3} P Specific conductance of acetone: 2.83 x 10^{-9} Ω^{-1} cm^{-1}

*At this point the stopcock slipped and doubt was introduced in the fourth digit; this error was present in the next two points but the relative uncertainty was not as great due to the much higher concentration.

are listed and the equivalent conductances are calculated utilizing the corrected specific conductances.[1] The tables also include the average of the absolute values of the deviations for the measured resistances.

A plot of the uncorrected specific conductance of lithium bromide versus the normality of lithium bromide is exhibited for Series I-V in Figure 7. The corrected specific conductance of lithium bromide as a function of the lithium bromide normality for Series I through IV is shown in Figures 8 and 9 and for Series I and V in Figure 10. The specific conductance of the system minus the specific conductance of the acetone is shown in Figure 11 as a function of the normality of the bromosuccinic acid for solutions which are 10^{-3}, 10^{-4}, 10^{-5} and zero normal with respect to lithium bromide; this is tantamount to correcting for the conductance of the acetone. Figure 12 gives the specific conductance of the system minus the specific conductance of the acetone and lithium bromide as a function of the normality of the bromosuccinic acid for solutions which have normalities with respect to lithium bromide of 10^{-3}, 10^{-4}, 10^{-5} and zero; this is equivalent to subtracting the specific conductance obtained in Series I from the specific conductance of the solution. Figure 13 shows the corrected specific conductance of bromosuccinic acid in acetone as a function of its concentration.

Treatment of Data With Fuoss-Onsager-Skinner Equation

Fuoss, Onsager and Skinner (136) outlined a means of programming

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[1]The uncorrected specific conductance is the specific conductance of the solution; the corrected specific conductance is the difference between the specific conductance of the solution and the specific conductance of the solvent.

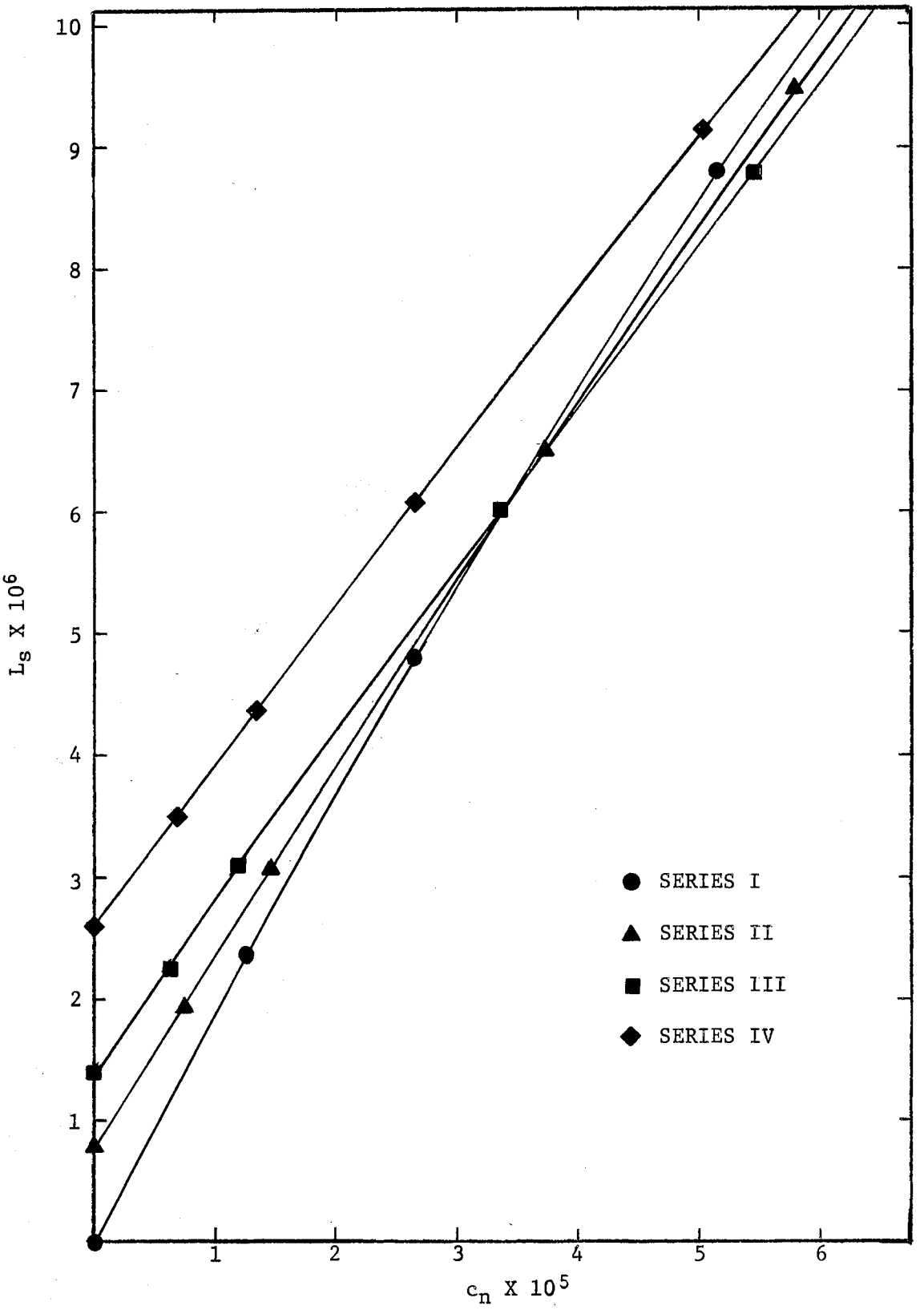

Figure 7. Uncorrected Specific Conductance of Lithium Bromide as a Function of Lithium Bromide Concentration for Series I-IV

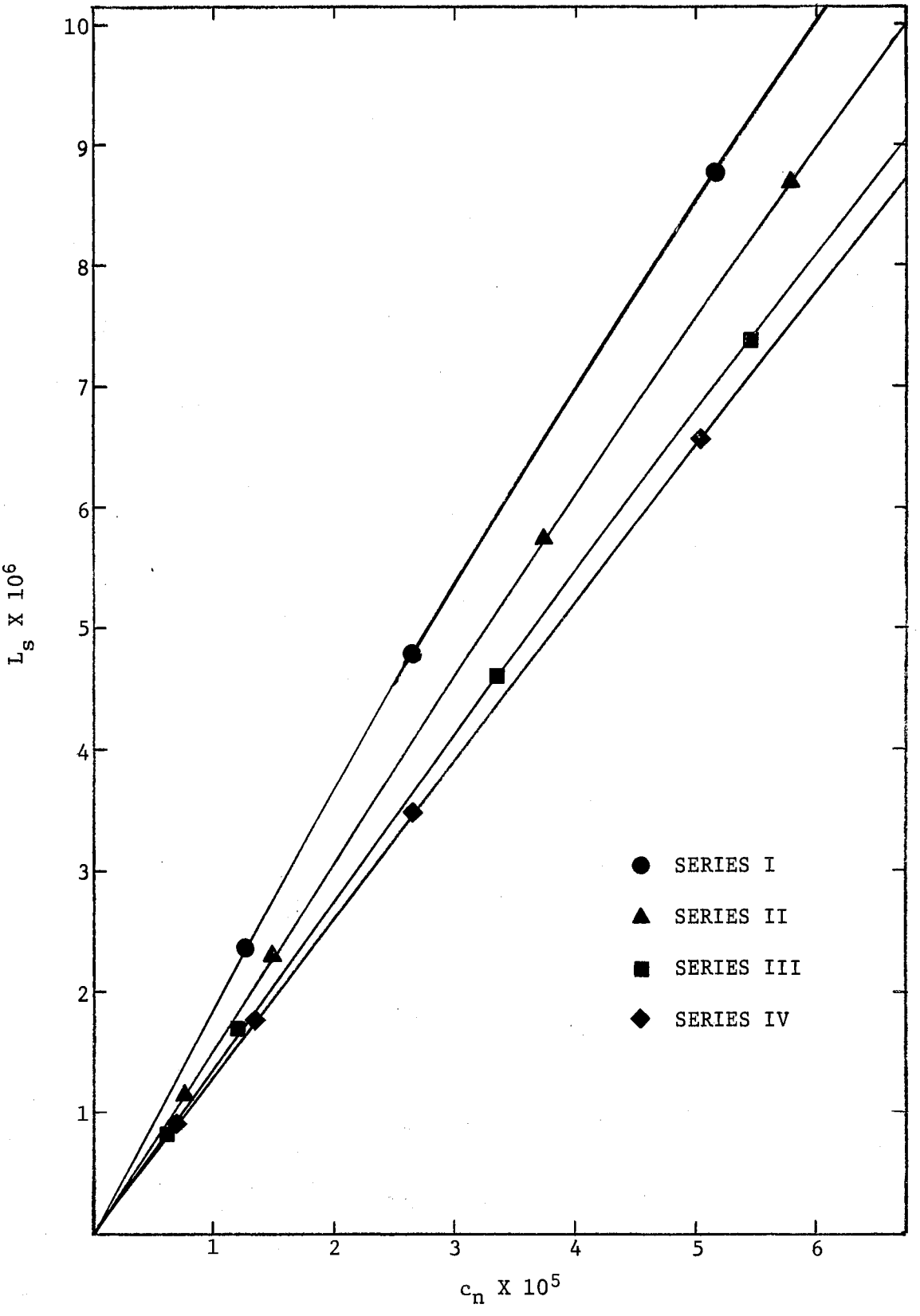

Figure 8. Corrected Specific Conductance of Lithium Bromide as a Function of Lithium Bromide Concentration for Series I-IV

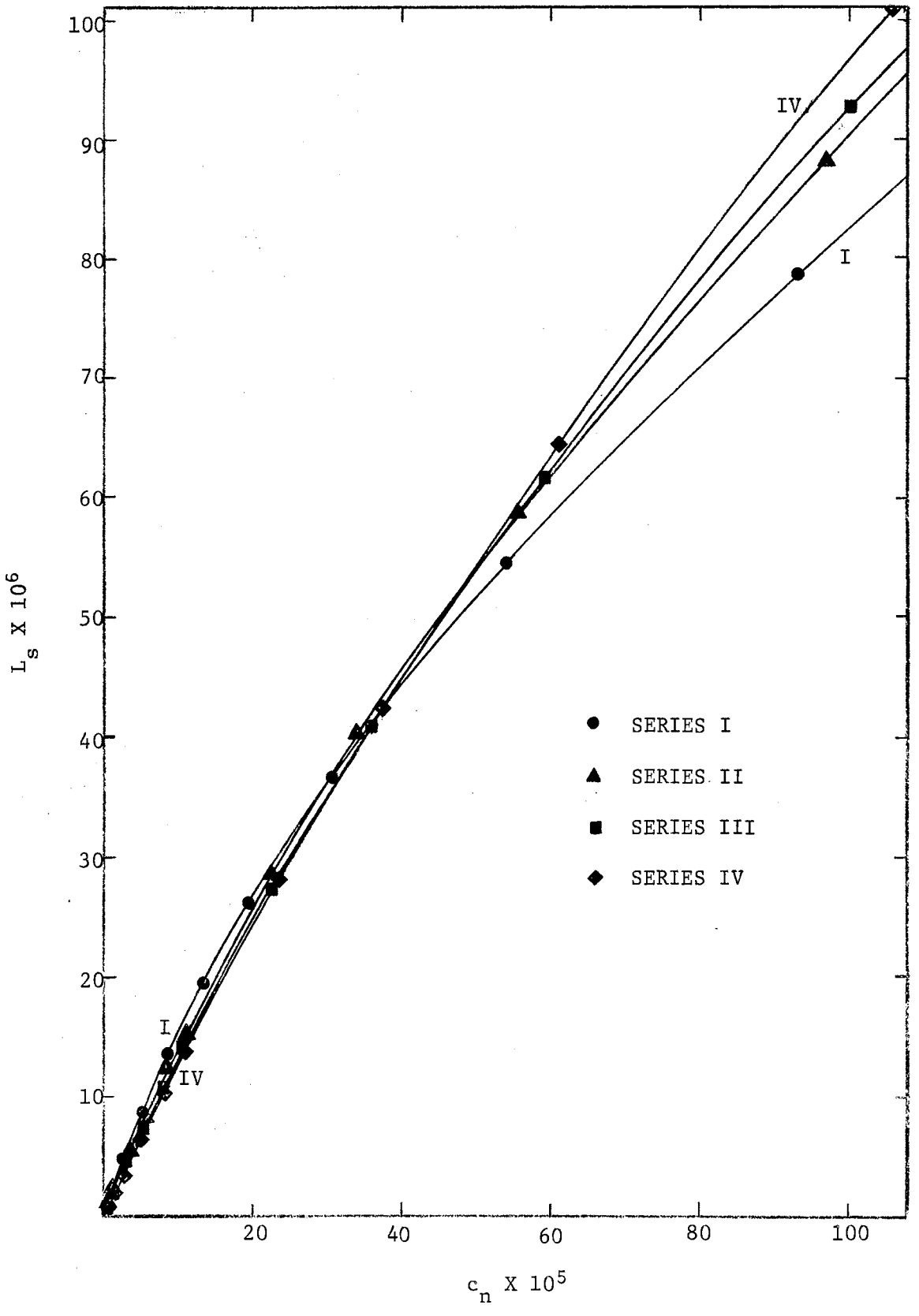

Figure 9. Corrected Specific Conductance of Lithium Bromide as a Function of Lithium Bromide Concentration for Series I-IV

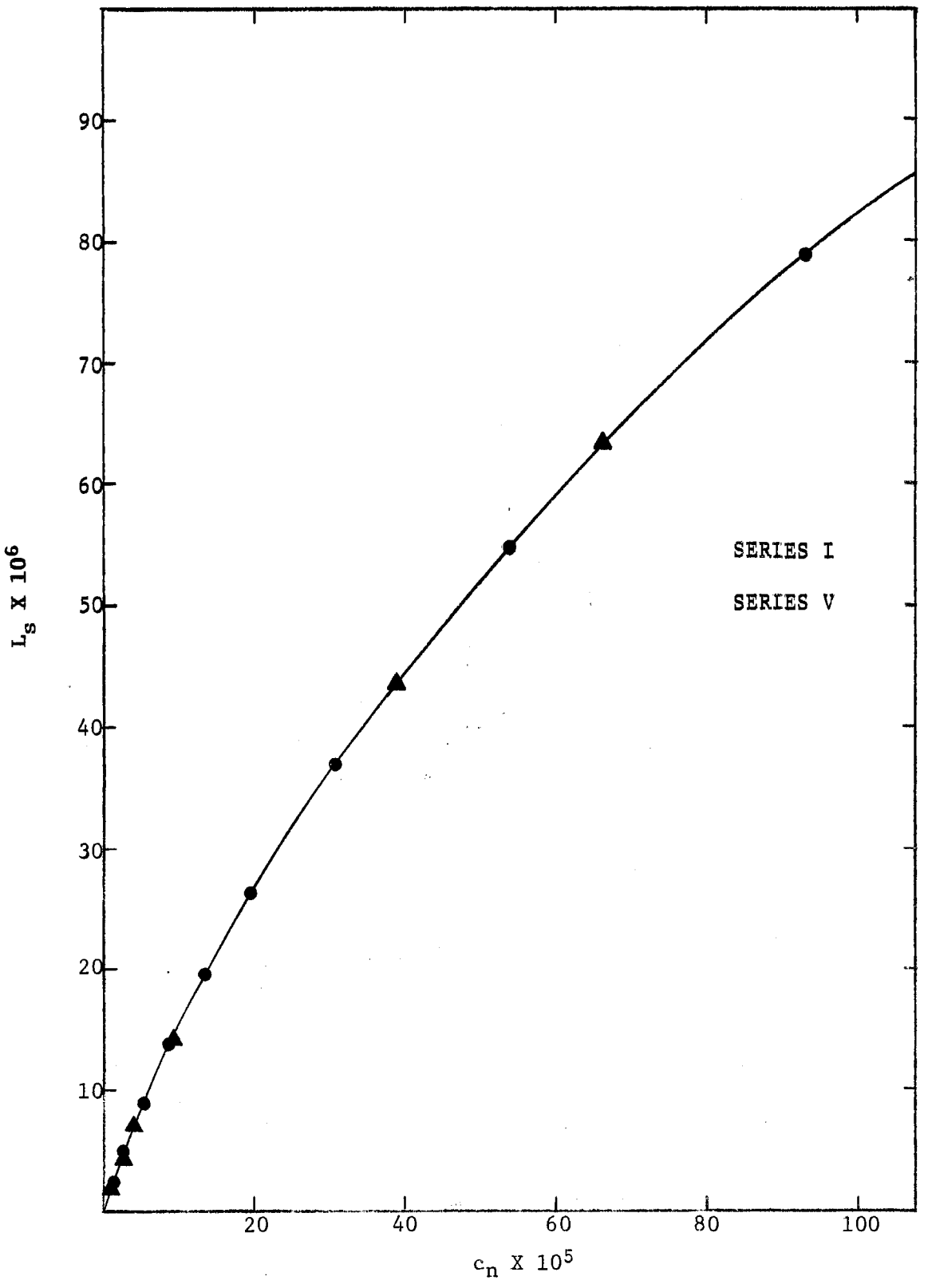

Figure 10. Corrected Specific Conductance of Lithium Bromide as a Function of Lithium Bromide Concentration for Series I and V

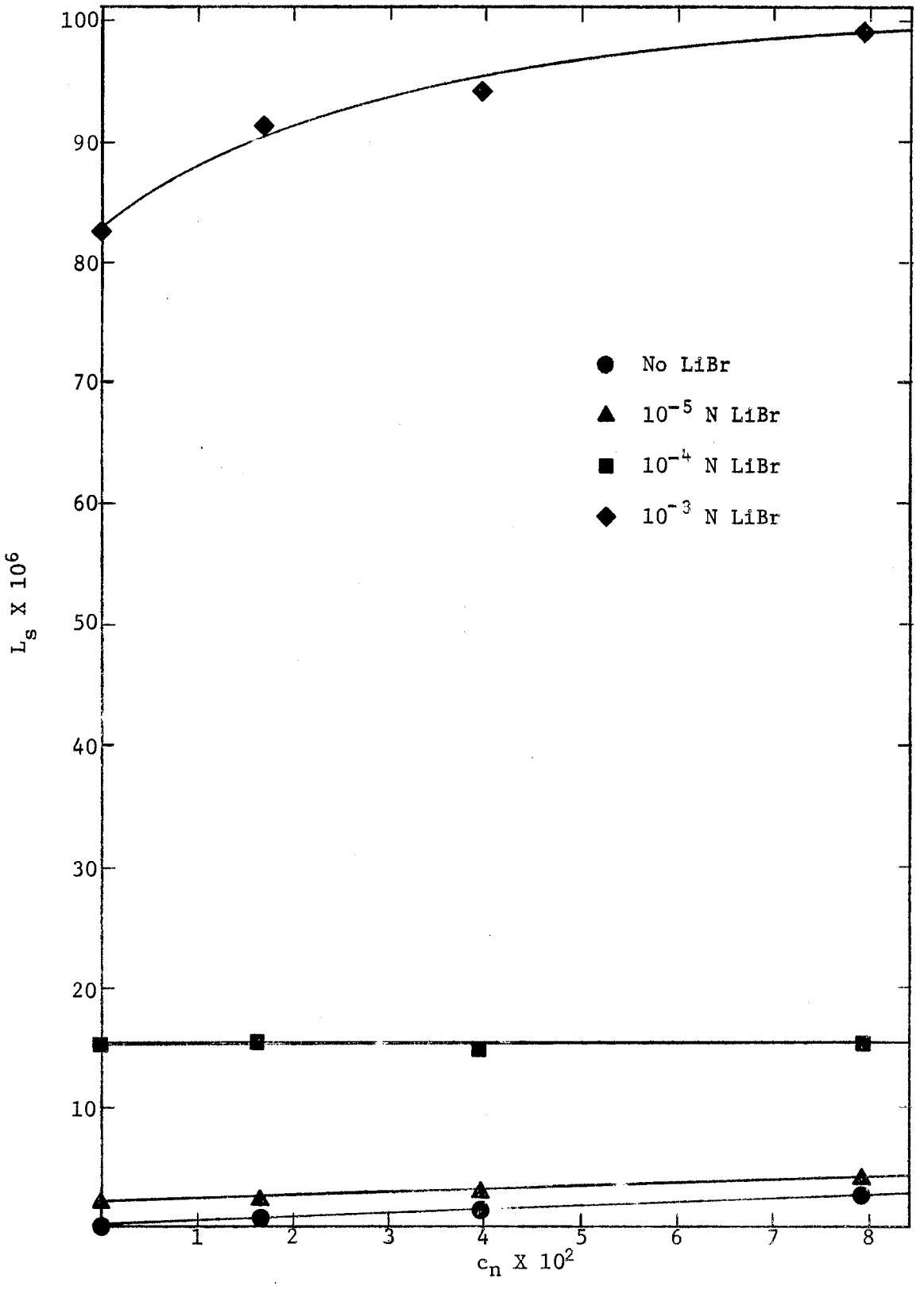

Figure 11. Specific Conductance of Solution Minus Specific Conductance of Acetone as a Function of Bromosuccinic Acid Concentration for Various Fixed Amounts of Lithium Bromide

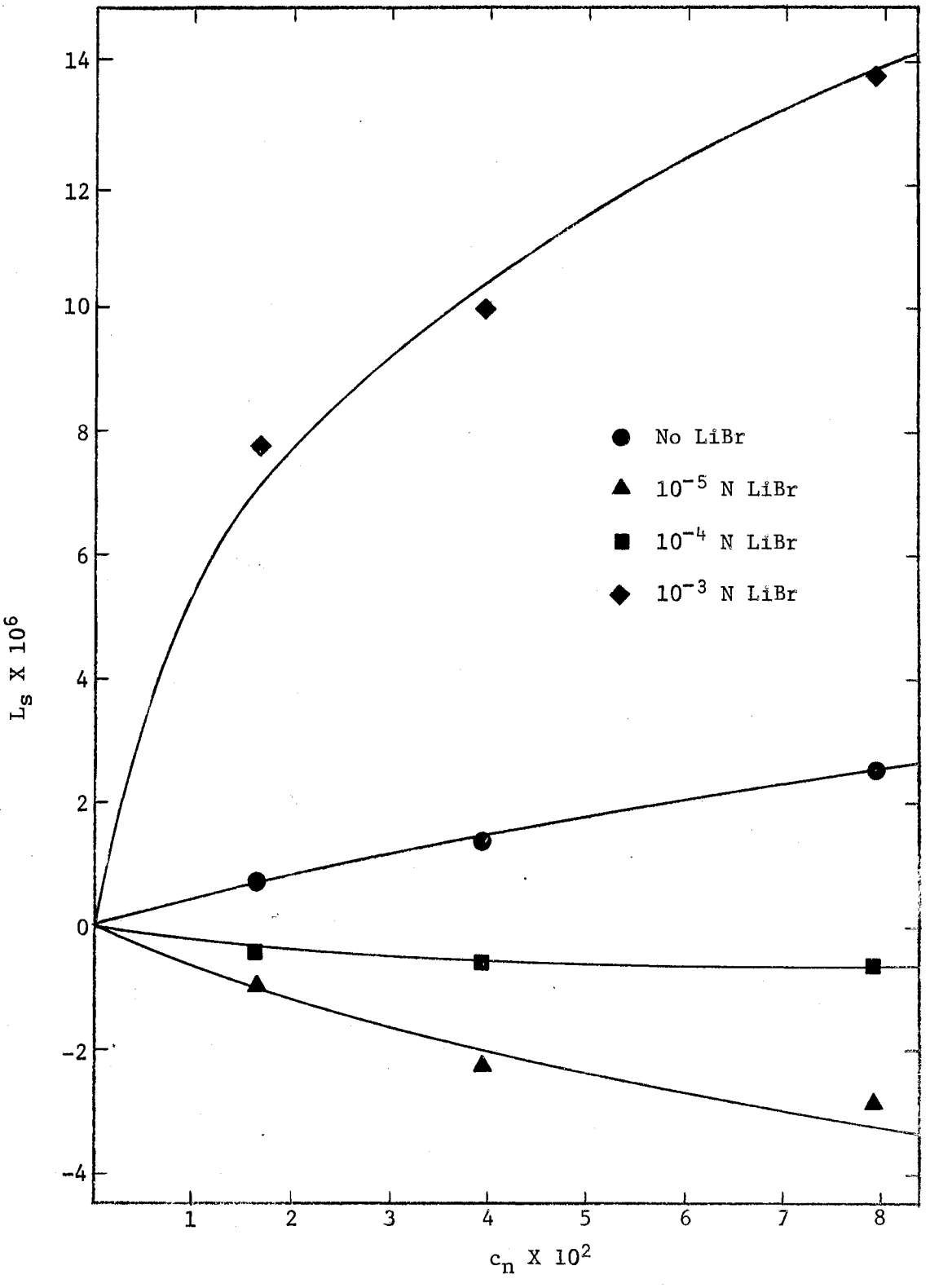

Figure 12. Specific Conductance of Solution Minus Specific Conductance of Acetone and Lithium Bromide as a Function of Bromosuccinic Acid Concentration for Various Fixed Amounts of Lithium Bromide

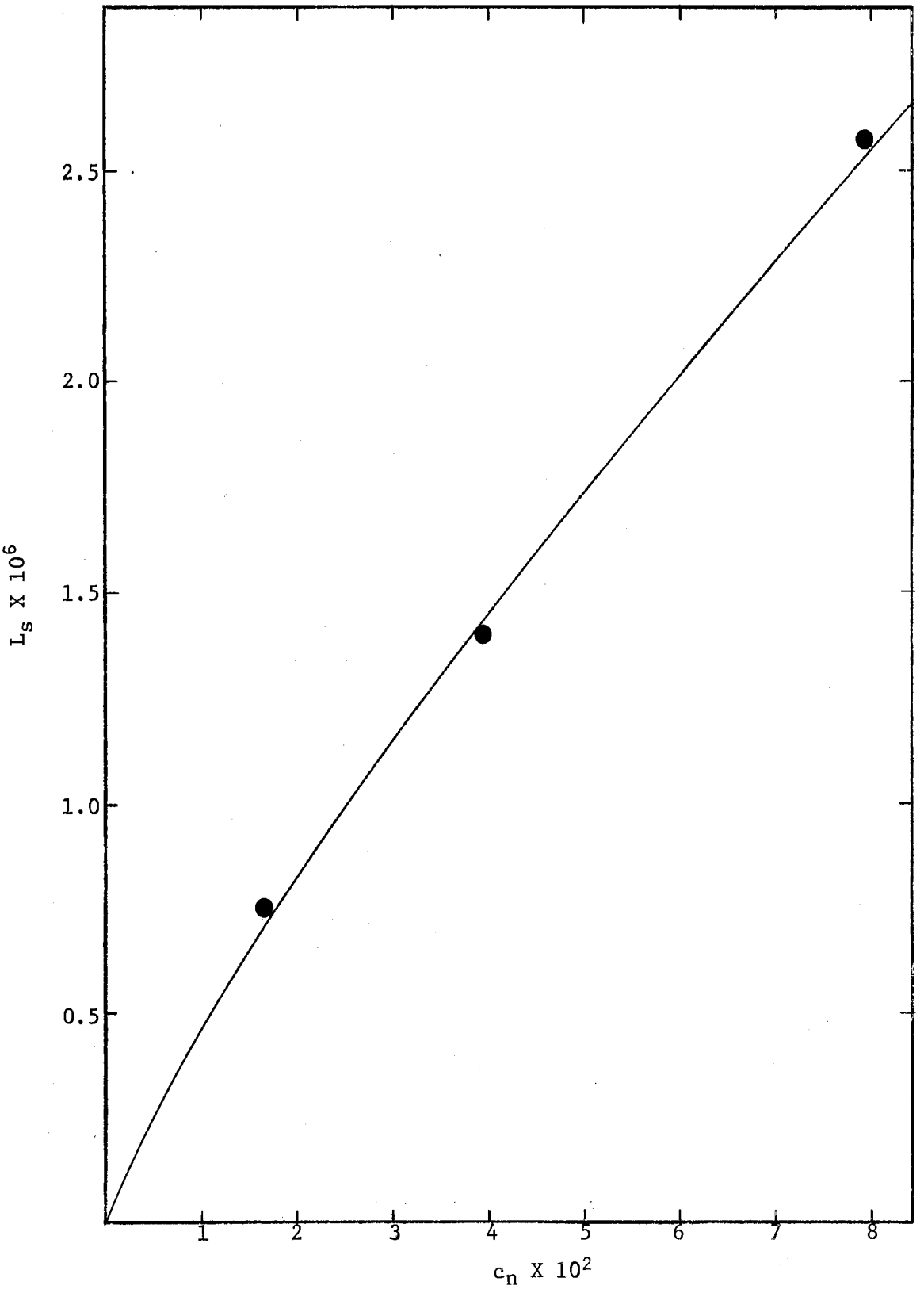

Figure 13. Corrected Specific Conductance of Bromosuccinic Acid in Acetone as a Function of Bromosuccinic Acid Concentration

the FOS equation--Equation (1-120)--in order to obtain the three parameters, $\underline{\Lambda_o}$, $\underline{L}$ and $\underline{K_A}$, from the data. The outline follows:

> A preliminary value of $\underline{\Lambda_o}$ is obtained by graphical extrapolation, and estimates (which need not be at all accurate) of $\underline{L}$ and $\underline{K_A}$ are made. As zeroth approximation, $\underline{\gamma}$ is set equal to the conductance ratio $\underline{\Lambda/\Lambda_o}$ in the square root term [of Equation (1-120)], giving as a first approximation
>
> $$\gamma_1 = \Lambda/[\Lambda_o - S(c\Lambda/\Lambda_o)^{1/2}]. \qquad (6\text{-}1)$$
>
> Since the linear and logarithmic terms usually just about cancel each other, [Equation (6-1)] is already a fair approximation. (If the estimated $\underline{\Lambda_o}$ is too small, the denominator of [Equation (6-1)] can become negative, and then [Equation (6-2)], which calls for the square root of $c\gamma_1$, would set the computer off on an infinite loop. To avoid this trap, an IF instruction terminates the computation, should γ_1 come out negative.) Then as next approximation
>
> $$\gamma_2 = \Lambda/[\Lambda_o - Sc^{1/2}\gamma_1^{1/2} + Ec\gamma_1 \log_{10}(6E_1' c\gamma_1) + Lc\gamma_1]. \qquad (6\text{-}2)$$
>
> This process is iterated until the condition
>
> $$|\gamma_n - \gamma_{n-1}| < 0.00005 \qquad (6\text{-}3)$$
>
> is satisfied. Then, if the converged value of $\underline{\gamma}$ is less than unity, the data are treated by the conventional least-squares program to obtain $\underline{\Lambda_o}$, $\underline{L}$, and $\underline{K_A}$. From both $\underline{L}$ and $\underline{K_A}$, values of $\underline{b}$ are obtained by solving [Equations (1-25) and (1-129)]. To avoid possible loops (and wasted machine time), the solution of $\underline{L_2(b)}$ for $\underline{b}$ is terminated if $\underline{b}$ becomes less than 1 (which would correspond to absurdly large $\underline{a}$ values). The function $\exp(\underline{b})/\underline{b}^3$ has a minimum at $\underline{b} = 3$; to avoid presenting the machine with the dilemma of a double-valued function and the probable attempt to divide by zero, the calculation of $\underline{b}$ from $\underline{K_A}$ is stopped if $\underline{b}$ becomes less than 3.05. The value at the minimum of $\exp(\underline{b})/\underline{b}^3$ is $\exp(3)/27 \simeq 0.75$. If the corresponding experimental value from $\underline{K_A}$ is less than 0.75, the machine is instructed not to attempt a solution. Finally, the calculation is terminated if $\underline{b}$ exceeds 25 (which would correspond to absurdly small $\underline{a}$ values). For the range of dielectric constants where both $\underline{L}$ and $\underline{K_A}$ can be determined with relatively good precision, the values of $\underline{a}$ from $\underline{L_2}$ and from $\underline{K_A}$ agree within about 10%; for high dielectric constants, the value from $\underline{K_A}$ becomes unreliable, while for low dielectric constants, the value from $\underline{L_2}$ becomes uncertain, as might be expected. If [Equation (6-2)] converges to a value greater than unity, $\underline{\gamma}$ is set equal to 1, and the solution of the three-parameter equation is continued. Then the data are automatically processed by the two-parameter

equation

$$\Lambda = \Lambda_o - Sc^{1/2} + Eclog_{10}(6E_1'c) + Lc. \qquad (6\text{-}4)$$

Also, if K_A from the three-parameter equation [Equation (1-120)] is less than 10, the data are analyzed by means of [Equation (6-4)].

A computer program for the solution of the FOS equation, using the above outline as a foundation, was written in Fortran IV through the joint efforts of Cunningham and the author. The program was constructed so as to be quite flexible. For example, with slight modification it could perform the calculations consecutively for more than one series or solve the two parameter equation rather than the three parameter equation. Also the trial values first assigned to b and K_A could be varied. The program was compiled and executed on the IBM System 360/50 (Operating System--H Level) computer. The listing of the computer program is given in Appendix D.

The initial input consists of the identification of and number of points in the series, the cell constant, and the temperature, viscosity, dielectric constant and specific conductance of the solvent. This is followed by the measured concentration and resistance of the solution for each point in the series. If a shunt is used in a measurement, its resistance is also included and the resistance of the solution is calculated from Equation (4-3).

Numerical values of α, β_o, E_1' and E_2' are computed from Equations (1-126), (1-127), (1-130) and (1-131), respectively. The specific conductance for each point is calculated from Equation (4-4); if the corrected specific conductance is desired the specific conductance of the solvent is subtracted from this. The equivalent conductance for each point is obtained from Equation (1-2) and a preliminary value of Λ_o is

gotten by applying a linear least squares to the phoreogram for Points II-V and determining the intercept. This estimate of Λ_o is used to calculate the Onsager tangent from Equation (1-46) and E' from Equation (1-100). The ratio of Λ to the preliminary value of Λ_o serves as a zeroth approximation for γ for each point; this is tantamount to Equation (1-77) with g equal to unity. The sum of the first two terms of the FOS equation using the first estimate of Λ_o and the zeroth approximation of γ is calculated for each point. If any point yields a nonpositive value for the sum, the computation is terminated and a message printed stating the reason. If all sums are positive, they are substituted for the denominator in Equation (6-1) to acquire a first approximation of γ for each point. (This is equivalent to solving Equation (1-76) for the γ outside the parentheses with Λ/Λ_o substituted for the γ inside the parentheses.) An estimate of L is obtained from Equation (1-121) by assuming a value of ten for b. The first four terms of the FOS equation are used in the denominator of Equation (6-2) to obtain a second approximation of γ for each point from the corresponding first approximation. More refined approximations are procured by iterating Equation (6-2) until either $|\gamma_n - \gamma_{n-1}| < 0.00005$ or 50 iterations have been made. If 50 iterations are performed the execution of the program is terminated and a statement is printed telling which points do not converge. A trial value of 3000 is assigned to K_A. The product $c\gamma$ is calculated for each point and its standard deviation, $\sigma_{c\gamma}$, estimated as $0.002c\gamma$. The standard deviation of the equivalent conductance, σ_Λ, for each point is taken to be 0.002Λ.

The appropriate values of arguments are passed from the main program to the subroutine subprogram for treatment of the data by the

method of least squares to evaluate Λ_o, L and K_A. The subroutine is based on the discussion by Wentworth (227) of least squares computations for curve fitting. The condition equations take the form of Equation (1-135); that is,

$$F_i[(c\gamma)_i, \Lambda_i, \Lambda_o, L, K_A] = 0, \tag{6-5}$$

in which the subscript, i, refers to the ith pair of measurements. These equations are obtained from Equation (1-120) with $f_{\pm}$ obtained from Equation (1-116) and τ given by Equation (1-101):

$$F_i = \Lambda_o - \Lambda_i - S(c\gamma)_i^{1/2} + E'(c\gamma)_i \log_e(\tau_i^2) + L(c\gamma)_i - K_A(c\gamma)_i \Lambda_i \exp(-2\tau_i). \tag{6-6}$$

The following partial derivatives are evaluated for each point:

$$F_{(c\gamma)_i} = \frac{\partial F_i}{\partial (c\gamma)_i} = -0.5S(c\gamma)_i^{-1/2} + E'\log_e(\tau_i^2) + E' + L - K_A\Lambda_i\exp(-2\tau_i) + K_A\tau_i\Lambda_i\exp(-2\tau_i), \tag{6-7}$$

$$F_{\Lambda_i} = \frac{\partial F_i}{\partial \Lambda_i} = -K_A(c\gamma)_i\exp(-2\tau_i) - 1, \tag{6-8}$$

$$F_{(\Lambda_o)_i} = \frac{\partial F_i}{\partial (\Lambda_o)_i} = 1 - \alpha(c\gamma)_i^{1/2} + E_1'(c\gamma)_i \log_e(\tau_i^2), \tag{6-9}$$

$$F_{L_i} = \frac{\partial F_i}{\partial L_i} = (c\gamma)_i \tag{6-10}$$

and

$$F_{(K_A)_i} = \frac{\partial F_i}{\partial (K_A)_i} = -(c\gamma)_i\Lambda_i\exp(-2\tau_i). \tag{6-11}$$

The weight of an observation, W_i, is defined as a quantity inversely proportional to the variance, σ_i^2; that is

$$W_i = \frac{\sigma_o^2}{\sigma_i^2}, \tag{6-12}$$

where $\underline{\sigma_o^2}$ is the variance of unit weight. The quantity $\underline{L_i}$ is defined by the equation,

$$L_i = \frac{F^2_{(c\gamma)_i}}{W_{(c\gamma)_i}} + \frac{F^2_{\Lambda_i}}{W_{\Lambda_i}}. \tag{6-13}$$

For each point, L_i is calculated from the equation,

$$L_i = \left(F_{(c\gamma)_i}\sigma_{(c\gamma)_i}\right)^2 + \left(F_{\Lambda_i}\sigma_{\Lambda_i}\right)^2; \tag{6-14}$$

this equation is the result of combining Equations (6-12) and (6-13) and assigning unity to $\underline{\sigma_o^2}$. The sum of the squares of the weighted residuals is calculated. The normal equations are

$$\sum_i \frac{F_{(\Lambda_o)_i} F_{(\Lambda_o)_i}}{L_i}\Delta\Lambda_o + \sum_i \frac{F_{(\Lambda_o)_i} F_{(K_A)_i}}{L_i}\Delta L + \sum_i \frac{F_{(\Lambda_o)_i} F_{L_i}}{L_i}\Delta K_A$$

$$= \sum_i \frac{F_{(\Lambda_o)_i} F_i}{L_i}, \tag{6-15}$$

$$\sum_i \frac{F_{(K_A)_i} F_{(\Lambda_o)_i}}{L_i}\Delta\Lambda_o + \sum_i \frac{F_{(K_A)_i} F_{(K_A)_i}}{L_i}\Delta L + \sum_i \frac{F_{(K_A)_i} F_{L_i}}{L_i}\Delta K_A$$

$$= \sum_i \frac{F_{(K_A)_i} F_i}{L_i} \tag{6-16}$$

and

$$\sum_i \frac{F_{L_i} F_{(\Lambda_o)_i}}{L_i}\Delta\Lambda_o + \sum_i \frac{F_{L_i} F_{(K_A)_i}}{L_i}\Delta L + \sum_i \frac{F_{L_i} F_{L_i}}{L_i}\Delta K_A$$

$$= \sum_i \frac{F_{L_i} F_i}{L_i}. \tag{6-17}$$

The coefficients of $\underline{\Delta\Lambda_o}$, $\underline{\Delta L}$ and $\underline{\Delta K_A}$ form the elements of the normal matrix. The inverse matrix is obtained and the change in each parameter is computed from its elements, $\underline{h_{ij}}$:

$$\Delta\Lambda_o = h_{11}\sum_i \frac{F_{(\Lambda_o)_i} F_i}{L_i} + h_{12}\sum_i \frac{F_{(K_A)_i} F_i}{L_i} + h_{13}\sum_i \frac{F_{L_i} F_i}{L_i}, \tag{6-18}$$

$$\Delta L = h_{21}\sum_i \frac{F_{(\Lambda_o)_i} F_i}{L_i} + h_{22}\sum_i \frac{F_{(K_A)_i} F_i}{L_i} + h_{23}\sum_i \frac{F_{L_i} F_i}{L_i} \tag{6-19}$$

and

$$\Delta K_A = h_{31}\sum_i \frac{F_{L_i} F_i}{L_i} + h_{32}\sum_i \frac{F_{(K_A)_i} F_i}{L_i} + h_{33}\sum_i \frac{F_{L_i} F_i}{L_i}. \tag{6-20}$$

The least squares estimate of each parameter is then found by subtracting this change from the previous estimate. The standard deviations of the parameters ($\underline{\sigma_{\Lambda_o}}$, $\underline{\sigma_L}$ and $\underline{\sigma_{K_A}}$) are also calculated along with the external estimate of the variance, $\underline{\sigma^2_{ext}}$. This estimate is the ratio of the sum of the squares of the weighted residuals to the number of degrees of freedom; the number of degrees of freedom is the number of pairs of observations minus the number of parameters (three) being determined. If the change in the sum of the squares of the weighted residuals is greater than 0.1 percent the entire subroutine is repeated. If not, the new argument values are transferred to the main program.

The Onsager tangent is recalculated from Equation (1-46) with the new approximation for $\underline{\Lambda_o}$. Equation (1-128) is solved for $\underline{a}$,

$$a = \frac{1.671\text{x}10^{-3}}{bDT}, \tag{6-21}$$

and substituted in Equation (1-129), which is rearranged and written as

$$\frac{eb}{b^3} = \frac{K_A}{2.523\text{x}10^{21}}\left(\frac{DT}{16.71\text{x}10^{-4}}\right)^3. \tag{6-22}$$

The logarithm of both sides is taken and the equation is set up for iteration:

$$b_n = \log_e\left[\frac{K_A}{2.523\times10^{21}}\left(\frac{DT}{16.71\times10^{-4}}\right)^3\right] - 3\log_e(b_{n-1}). \qquad (6\text{-}23)$$

The iteration is carried out if $3.05 \leq b \leq 25$ until $|b_n - b_{n-1}| < 0.001$, which gives the value of b calculated from the experimental K_A and Equation (1-129). This value of b is used to compute a from Equation (6-21) and L from Equation (1-121). A new estimate of L is obtained by taking the average of the value of L which was last transferred into the subprogram and the value returned from the subprogram. This new estimate of L is used to gain a new approximation for γ for each point by iteration of Equation (6-2) until $|\gamma_n - \gamma_{n-1}| < 0.00005$. If the difference between this new value for γ and the previous value for γ for any point is greater than 0.0005, E' is re-evaluated from Equation (1-100) using the most recent approximation for Λ_o. The product $(c\gamma)_i$ is computed for each point along with its standard deviation, which is still taken to be $0.002(c\gamma)_i$. The data are again treated by the least squares subprogram and the computations of the beginning of this paragraph repeated. This procedure is repeated until the change in γ for each point due to the least squares treatment is less than 0.0005. The point with the maximum standard deviation is found and the ratio of its standard deviation to the average standard deviation is calculated. If the ratio is not less than two, the point is rejected with identification and the least squares treatment reapplied to the remaining points. If no points are rejected, values of L are calculated from Equation (1-121) by assigning integral values of one to 25 to b and using the least squares value of Λ_o.

The output includes the identification of the series, the cell constant, and the temperature, viscosity, dielectric constant and specific conductance of the solvent. The molar concentration, square root of the molar concentration, resistance, specific conductance and equivalent conductance of each point are tabulated. Values for α, β_o, E_1' and E_2' are given, as well as the first estimate for Λ_o and the estimate of L with the initial value assigned to b. For each point the zeroth and first approximation of γ are printed along with the refined approximation obtained from iteration of Equation (6-2). Each time the subprogram is called, values for each point for F_i, $F_{(\Lambda_o)_i}$, F_{L_i}, $F_{(K_A)_i}$, $F_{(c\gamma)_i}$, F_{Λ_i}, L_i, F_i^2/L_i, γ_i, $(c\gamma)_i$, $\sigma_{(c\gamma)_i}$, σ_{Λ_i}, the S term, E term, L term, K_A term and the calculated equivalent conductance are listed. (The S term, E term, L term and K_A terms are given by the second through fifth terms, respectively, of the right side of Equation (1-120) and the calculated equivalent conductance is given by the sum of Λ_i and F_i.) Also on each call of the subprogram the elements of both the normal and inverse matrices, Λ_o, K_A, L, σ_{Λ_o}, σ_{K_A}, σ_L, $\Sigma F_i^2/L_i$, σ^2_{ext}, σ_{ext}, b (calculated from the experimental K_A and Equation (1-129)), a (calculated from b and Equation (6-21)) and L (calculated from b and Equation (1-121)) are given. Finally, the ratio of the maximum standard deviation to the average deviation is printed followed by a listing of integral values of b from one to 25 and the corresponding value of L calculated from Equation (1-121).

The parameters of the FOS equation are given in Table VIII for each series. The series is identified in the first column. The second, third and fourth columns list Λ_o, L and K_A, respectively, and their standard deviations, as calculated from the program. The next column

gives b as calculated from K_A and Equation (6-23). Values of a, expressed in Å, obtained from Equation (6-21) are entered in the last column.

TABLE VIII

CALCULATED CONSTANTS OF FOS EQUATION FOR LITHIUM BROMIDE FOR EACH SERIES

Series	Λ_o	L	K_A	b	a
I	198.14±0.90	-16 905±8357	3320±145	11.53	2.35
II	162.20±1.62	-19 781±15 040	982±254	9.83	2.75
III	143.47±0.50	-10 443±4876	500±84	8.84	3.06
IV	135.74±0.70	-10 036±6340	195±111	7.34	3.69
V	180.09±2.54	-56 567±39 330	1433±609	10.37	2.61

Tables IX-XIII give the numerical values of the terms in the theoretical equation for Series I-V, respectively. Each row shows the values calculated for a given point; the point is designated in the first column. The second column gives the values for γ. The values of the S term, E term, L term and K_A term of Equation (1-120) are tabulated in the next four columns, respectively. The seventh column contains the equivalent conductance calculated from Equation (1-120). (It should be noted that the calculated value of Λ is obtained by addition of the E term and L term to Λ_o and subtraction of the S term and K_A term.) The last column gives $\delta\Lambda$, which is the calculated equivalent conductance minus the experimental equivalent conductance. (The experimental equivalent conductances are given in Tables III-VII.)

TABLE IX

FUNCTIONS CALCULATED FROM FOS EQUATION
FOR SERIES I

Point	γ	S Term	E Term	L Term	K_A Term	Λ	$\delta\Lambda$
I2	0.957	2.37	-0.18	-0.20	7.06	188.33	1.32
I3	0.930	3.39	-0.33	-0.42	13.54	180.47	0.08
I4	0.886	4.62	-0.55	-0.77	22.99	169.22	-1.08
I5	0.833	5.80	-0.79	-1.22	32.75	157.59	-1.06
I6	0.777	6.97	-1.06	-1.76	42.43	145.92	-0.51
I7	0.723	8.12	-1.35	-2.39	51.49	134.79	0.05
I8	0.653	9.69	-1.77	-3.40	62.52	120.77	1.08
I9	0.569	11.95	-2.43	-5.17	76.24	102.35	0.75
I10	0.491	14.58	-3.23	-7.71	88.56	84.07	-0.66

TABLE X

FUNCTIONS CALCULATED FROM FOS EQUATION
FOR SERIES II

Point	γ	S Term	E Term	L Term	K_A Term	Λ	$\delta\Lambda$
II2	0.964	1.66	-0.09	-0.14	1.05	159.25	4.65
II3	0.986	2.35	-0.16	-0.29	2.09	157.30	0.14
II4	0.981	3.74	-0.36	-0.72	4.99	152.38	-1.98
II5	0.967	4.62	-0.51	-1.11	7.27	148.69	-2.15
II6	0.948	5.60	-0.69	-1.62	10.05	144.24	-2.06
II7	0.932	6.34	-0.84	-2.08	12.30	140.65	-1.85
II8	0.865	8.64	-1.37	-3.86	19.29	129.04	0.78
II9	0.820	10.35	-1.79	-5.54	24.40	120.11	1.55
II10	0.766	12.76	-2.43	-8.41	31.00	107.60	1.47
II11	0.706	16.19	-3.37	-13.55	38.97	90.13	-1.05

TABLE XI

FUNCTIONS CALCULATED FROM FOS EQUATION
FOR SERIES III

Point	γ	S Term	E Term	L Term	K_A Term	Λ	$\delta\Lambda$
III2	0.993	1.42	-0.07	-0.06	0.40	141.51	0.59
III3	0.986	2.02	-0.12	-0.13	0.79	140.42	1.17
III4	0.986	3.35	-0.28	-0.35	2.06	137.43	-0.07
III5	0.981	4.26	-0.42	-0.56	3.19	135.04	-0.61
III6	0.973	5.22	-0.59	-0.84	4.57	132.25	-0.94
III7	0.965	5.97	-0.73	-1.10	5.76	129.92	-1.05
III8	0.923	8.41	-1.24	-2.18	9.87	121.76	0.20
III9	0.892	10.45	-1.71	-3.36	13.45	114.51	0.36
III10	0.849	13.07	-2.35	-5.26	17.80	104.98	0.69
III11	0.805	16.54	-3.23	-8.42	22.87	92.41	-0.38

TABLE XII

FUNCTIONS CALCULATED FROM FOS EQUATION
FOR SERIES IV

Point	γ	S Term	E Term	L Term	K_A Term	Λ	$\delta\Lambda$
IV2	0.984	1.47	-0.07	-0.07	0.17	133.97	1.95
IV3	0.999	2.05	-0.12	-0.13	0.32	133.11	-0.17
IV4	0.989	2.88	-0.22	-0.26	0.61	131.76	0.80
IV5	0.997	3.98	-0.37	-0.50	1.13	129.76	-0.79
IV6	0.996	5.06	-0.55	-0.81	1.74	127.59	-1.26
IV7	0.994	5.87	-0.70	-1.09	2.26	125.82	-1.55
IV8	0.969	8.51	-1.25	-2.30	4.12	119.56	-0.33
IV9	0.945	10.59	-1.72	-3.56	5.65	114.22	0.88
IV10	0.926	13.38	-2.40	-5.69	7.73	106.55	0.75
IV11	0.905	17.39	-3.37	-9.61	10.40	94.97	-0.41

TABLE XIII

FUNCTIONS CALCULATED FROM FOS EQUATION
FOR SERIES V

Point	γ	S Term	E Term	L Term	K_A Term	Λ	$\delta\Lambda$
V2	0.968	2.01	-0.13	-0.54	2.21	175.20	3.42
V3	0.973	2.61	-0.20	-0.90	3.67	172.70	1.04
V4	0.975	3.27	-0.30	-1.42	5.62	169.48	-1.25
V5	0.962	4.12	-0.44	-2.26	8.55	164.72	-1.93
V6	0.934	5.10	-0.62	-3.46	12.20	158.70	-0.87
V7	0.924	6.01	-0.81	-4.81	16.14	152.31	-3.34
V8	0.742	11.10	-2.08	-16.38	34.46	116.07	4.35
V9	0.696	14.03	-2.92	-26.18	43.54	93.41	-2.05

A graph of γ as a function of lithium bromide molarity is shown in Figure 14 for Solvents I-IV; the concentration is plotted on a logarithmic scale in order that the entire range may be included. Figures 15-17 display Λ_o, K_A and a, respectively, for lithium bromide as a function of bromosuccinic acid molality in acetone; the parameter, a, is expressed in Å. The phoreograms for lithium bromide calculated from the FOS equation for Series I-IV are delineated in Figure 18. Figures 19-23 exhibit the experimental and calculated phoreograms for lithium bromide in Solvents I-V, respectively, and Figure 24 shows the calculated phorgrams for Series I and V.

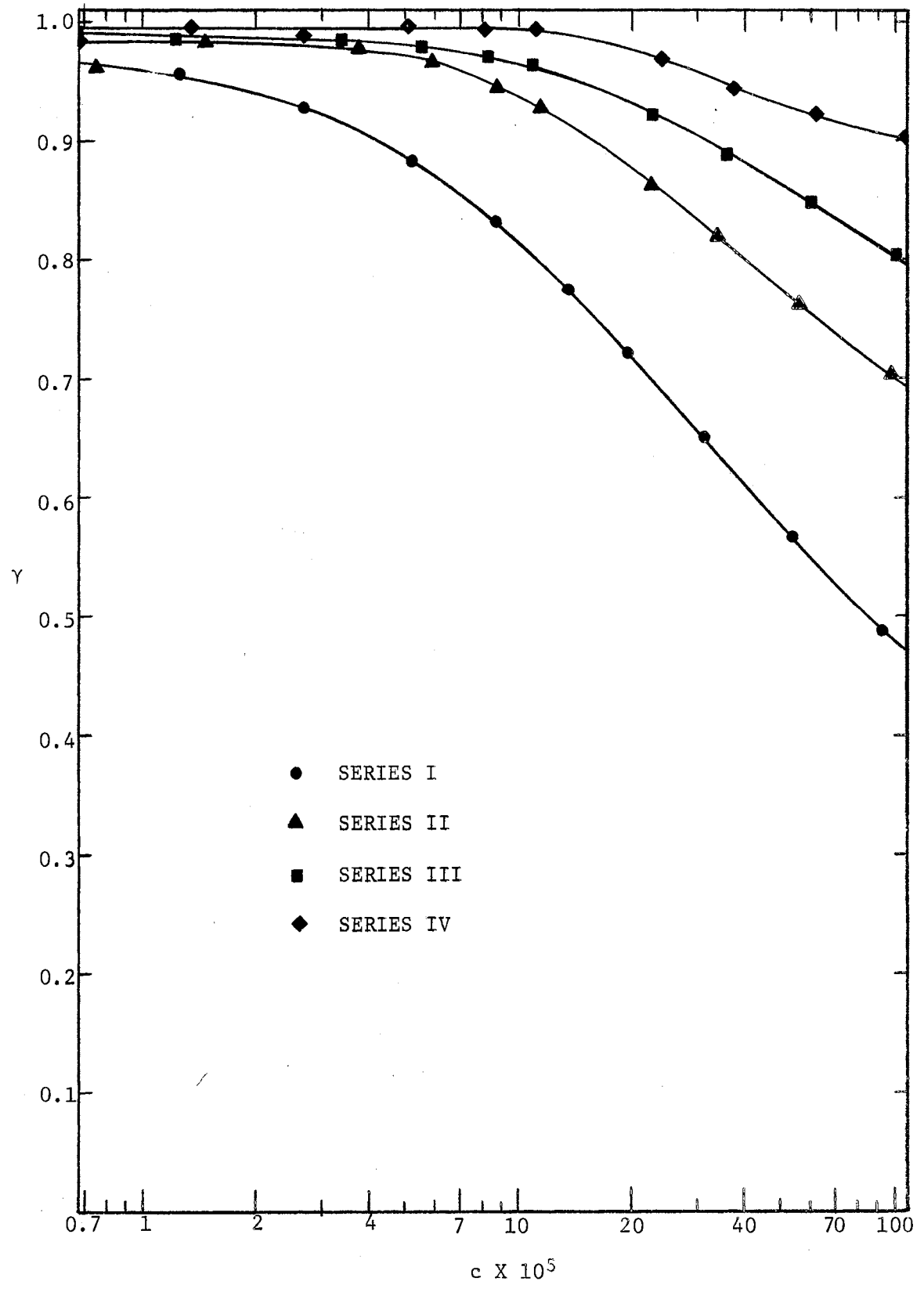

Figure 14. Fraction of Lithium Bromide Existing as Free Ions in Solvents I-IV as a Function of Lithium Bromide Concentration

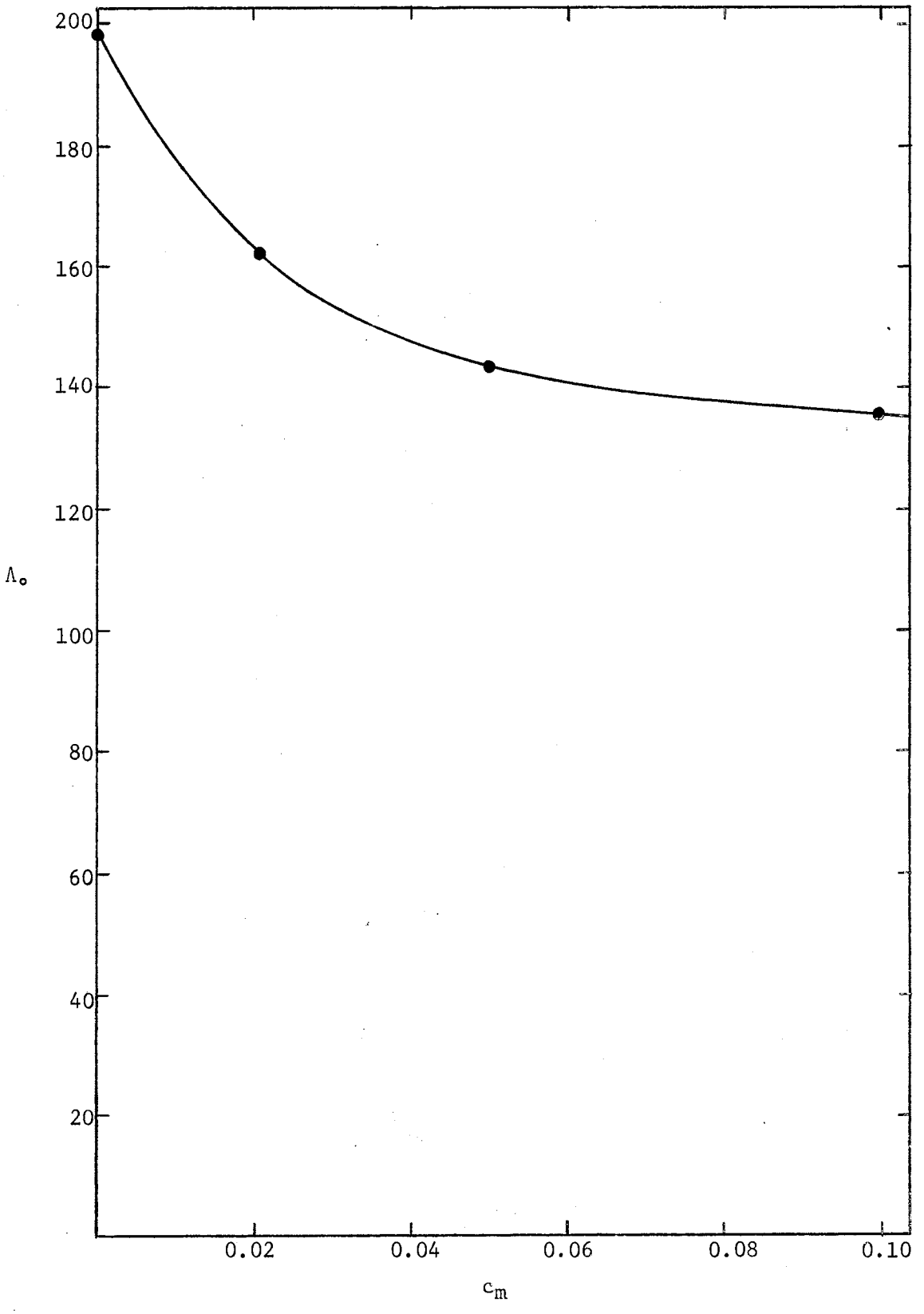

Figure 15. Equivalent Conductance at Infinite Dilution for Lithium Bromide in Acetone as a Function of Bromosuccinic Acid Concentration

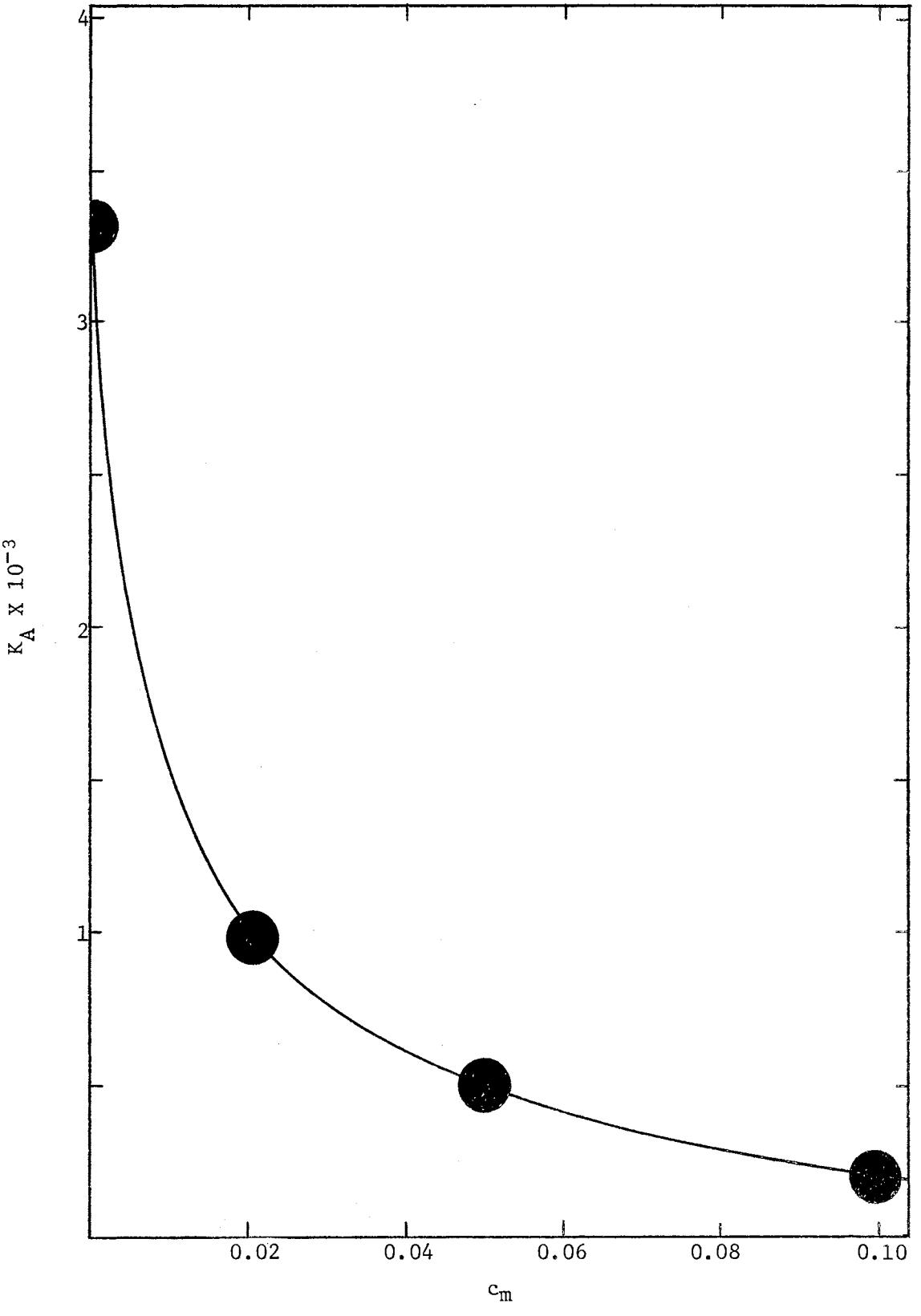

Figure 16. Association Equilibrium Constant for Lithium Bromide in Acetone as a Function of Bromosuccinic Acid Concentration

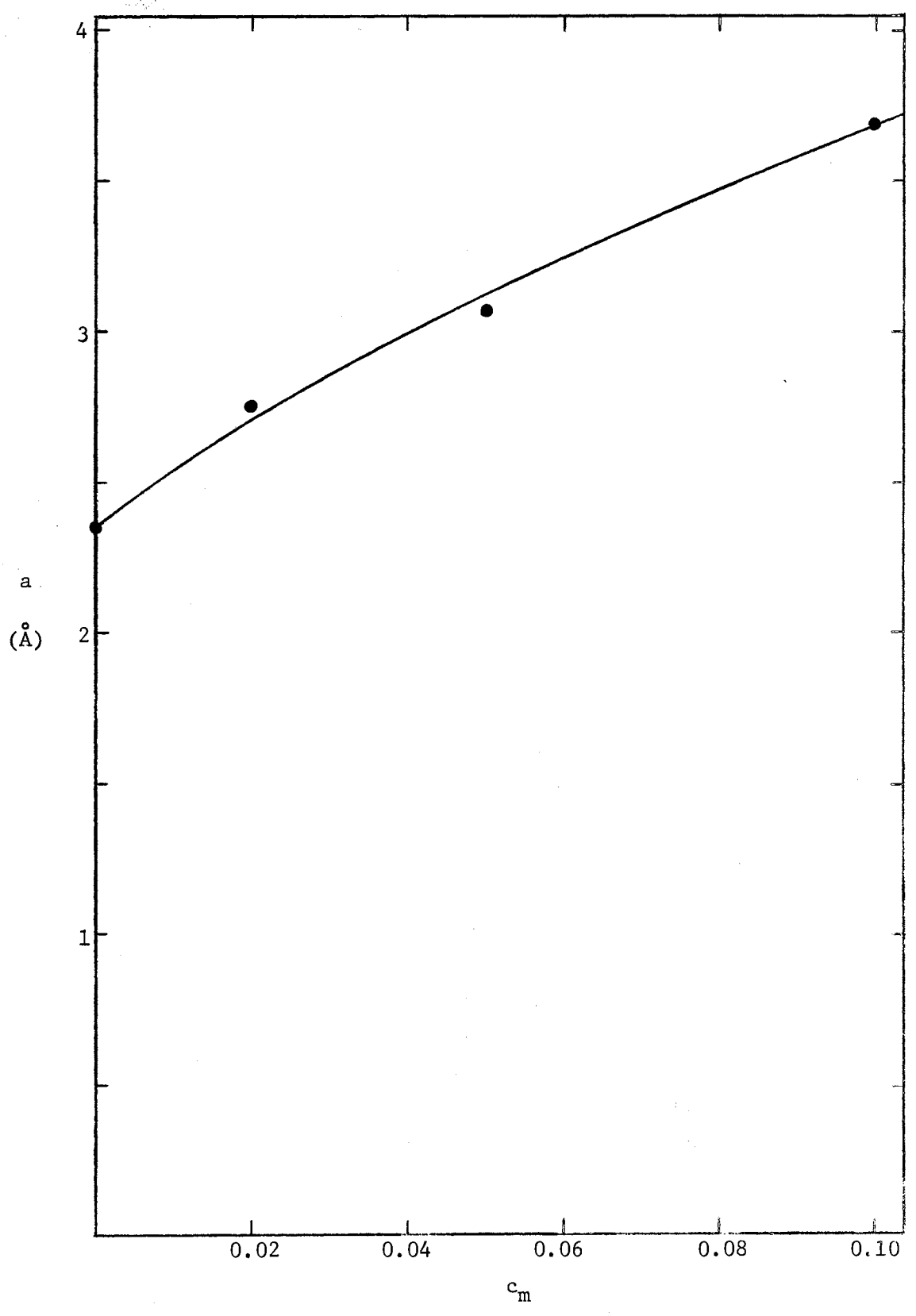

Figure 17. Sum of Ionic Radii for Lithium Bromide in Acetone as a Function of Bromosuccinic Acid Concentration

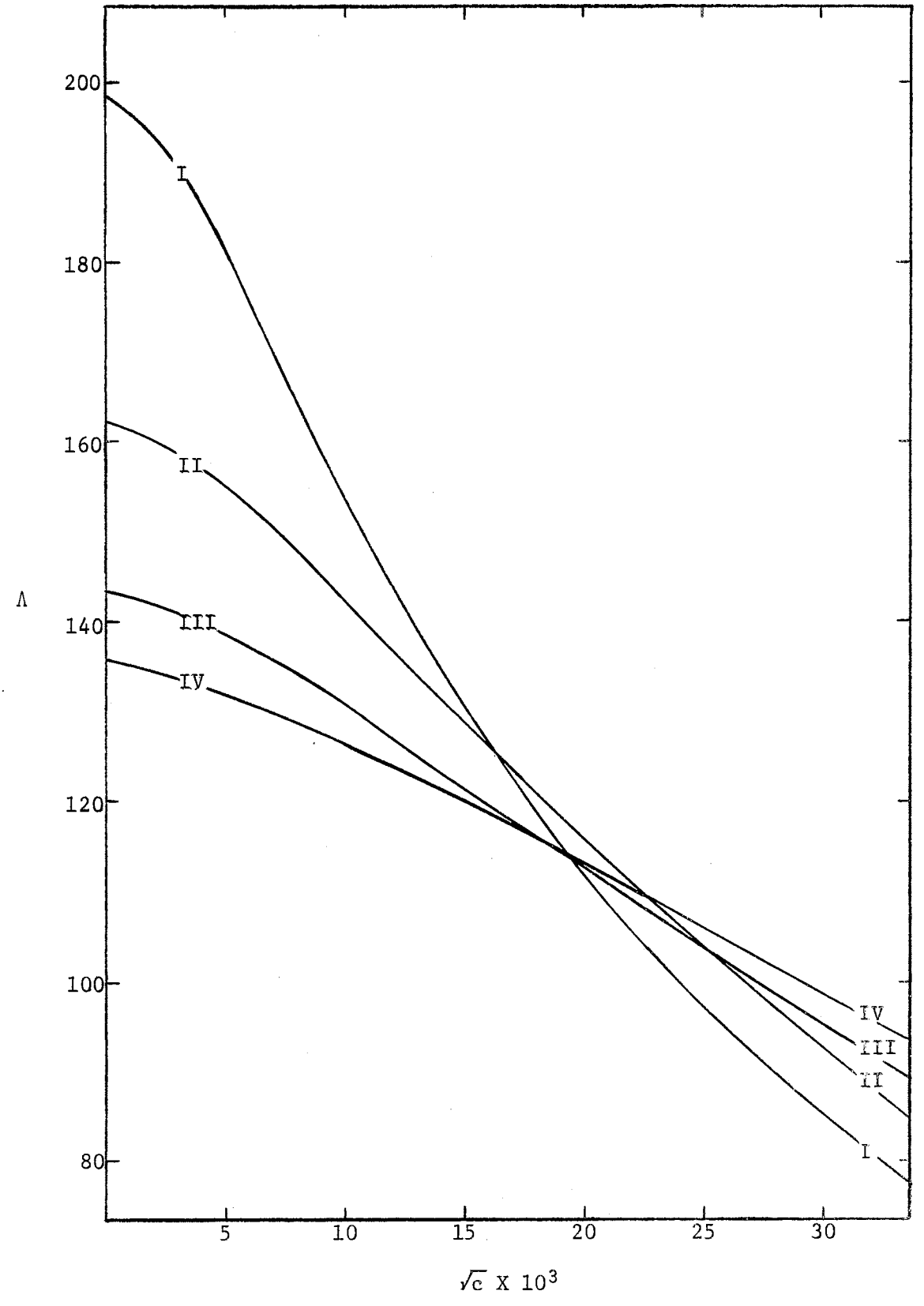

Figure 18. Lithium Bromide Phoreogram Calculated From the FOS Equation and Experimental Data for Solvents I-IV

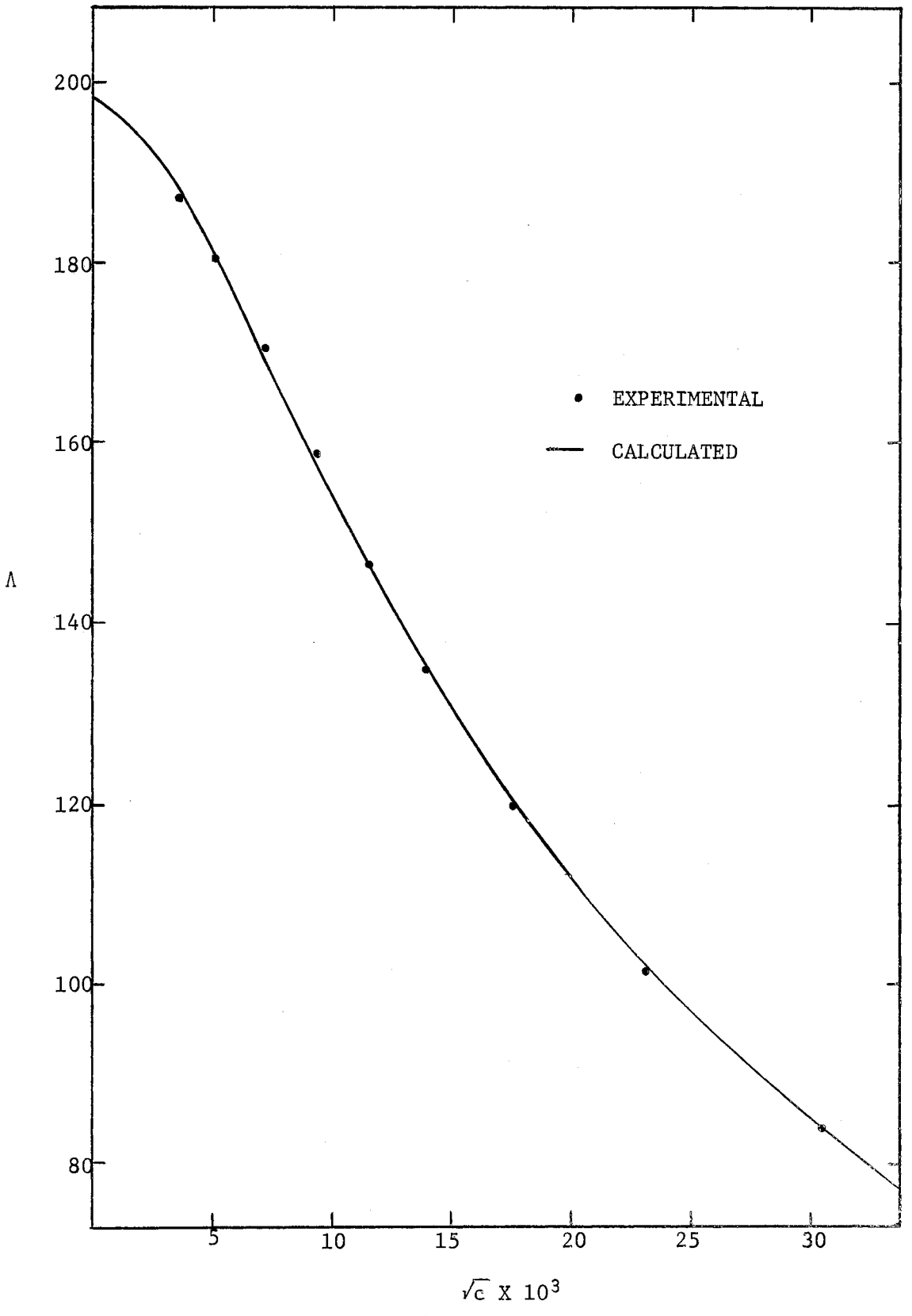

Figure 19. Phoreogram of Lithium Bromide in Acetone (Solvent I)

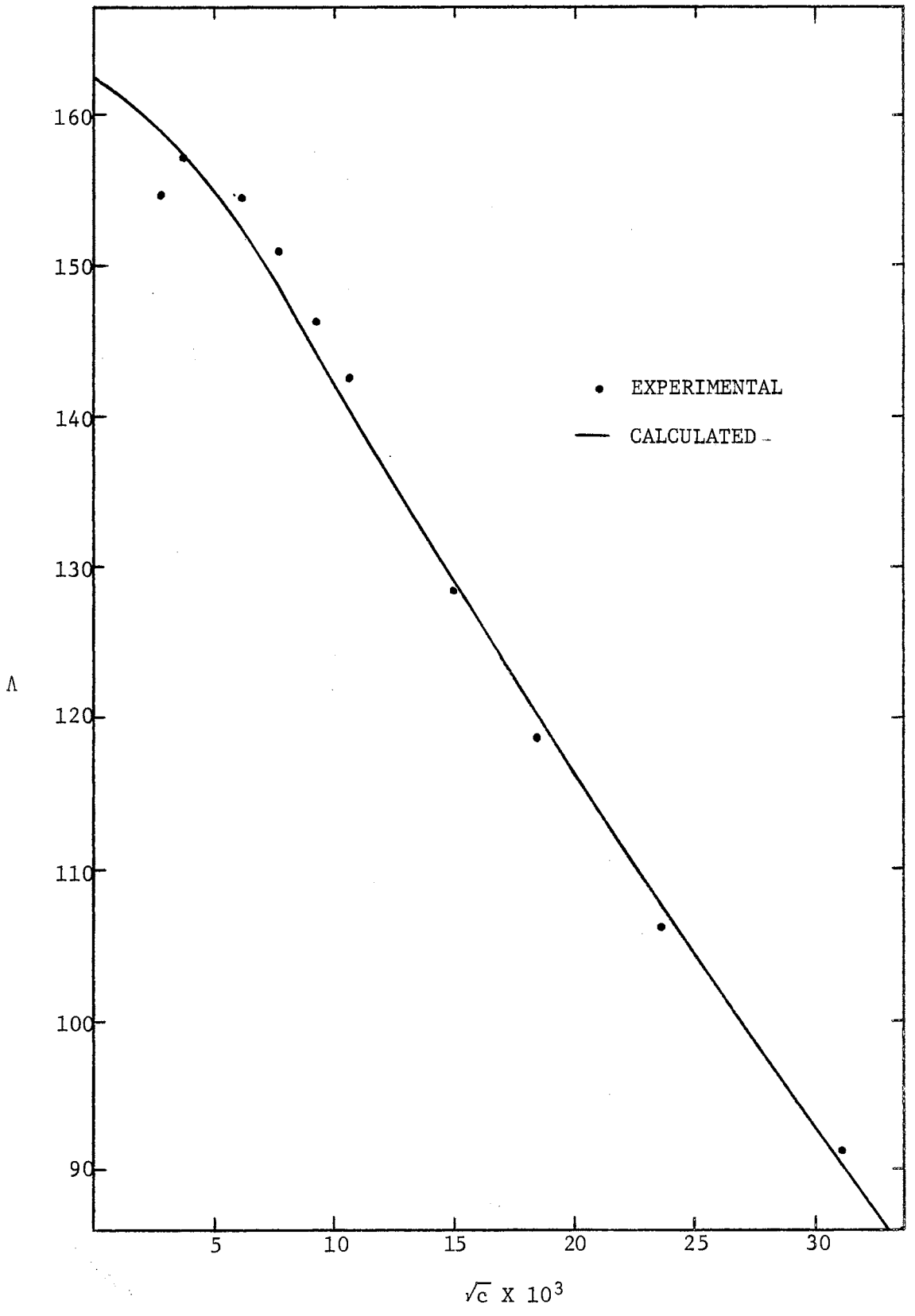

Figure 20. Phoreogram of Lithium Bromide in 0.02063 Molal Bromosuccinic Acid in Acetone (Solvent II)

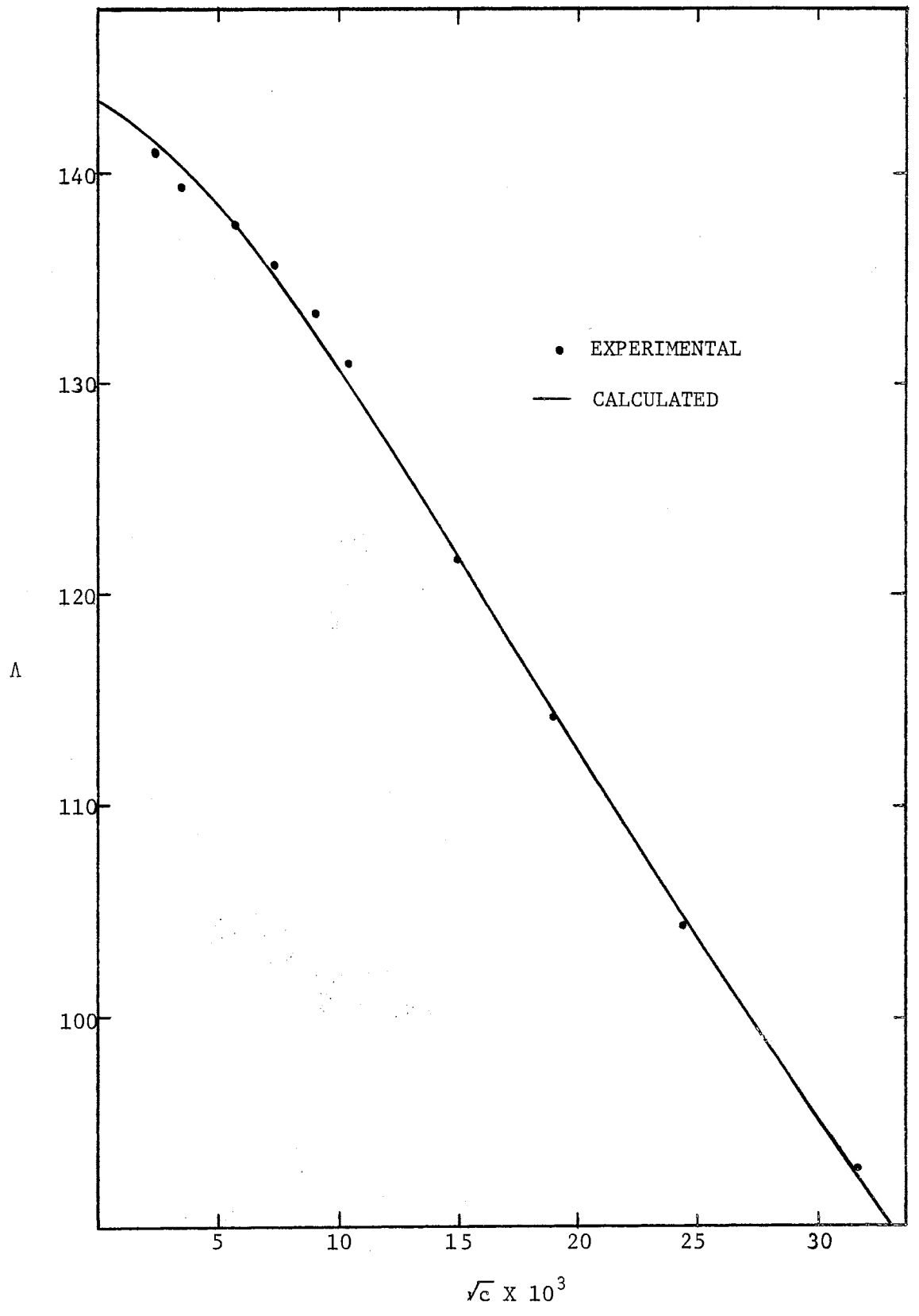

Figure 21. Phoreogram of Lithium Bromide in 0.05009 Molal Bromosuccinic Acid in Acetone (Solvent III)

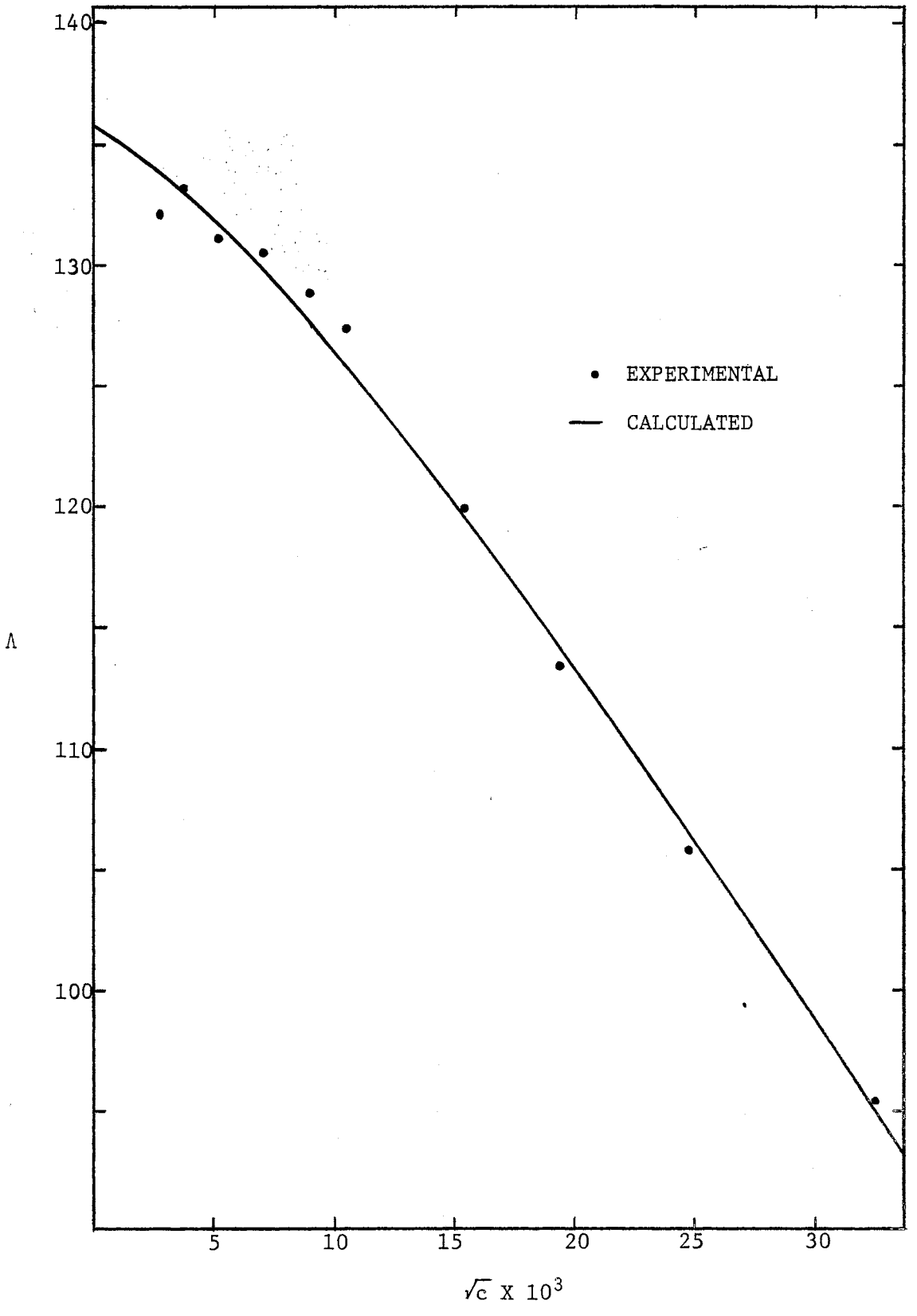

Figure 22. Phoreogram of Lithium Bromide in 0.09958 Molal Bromosuccinic Acid in Acetone (Solvent IV)

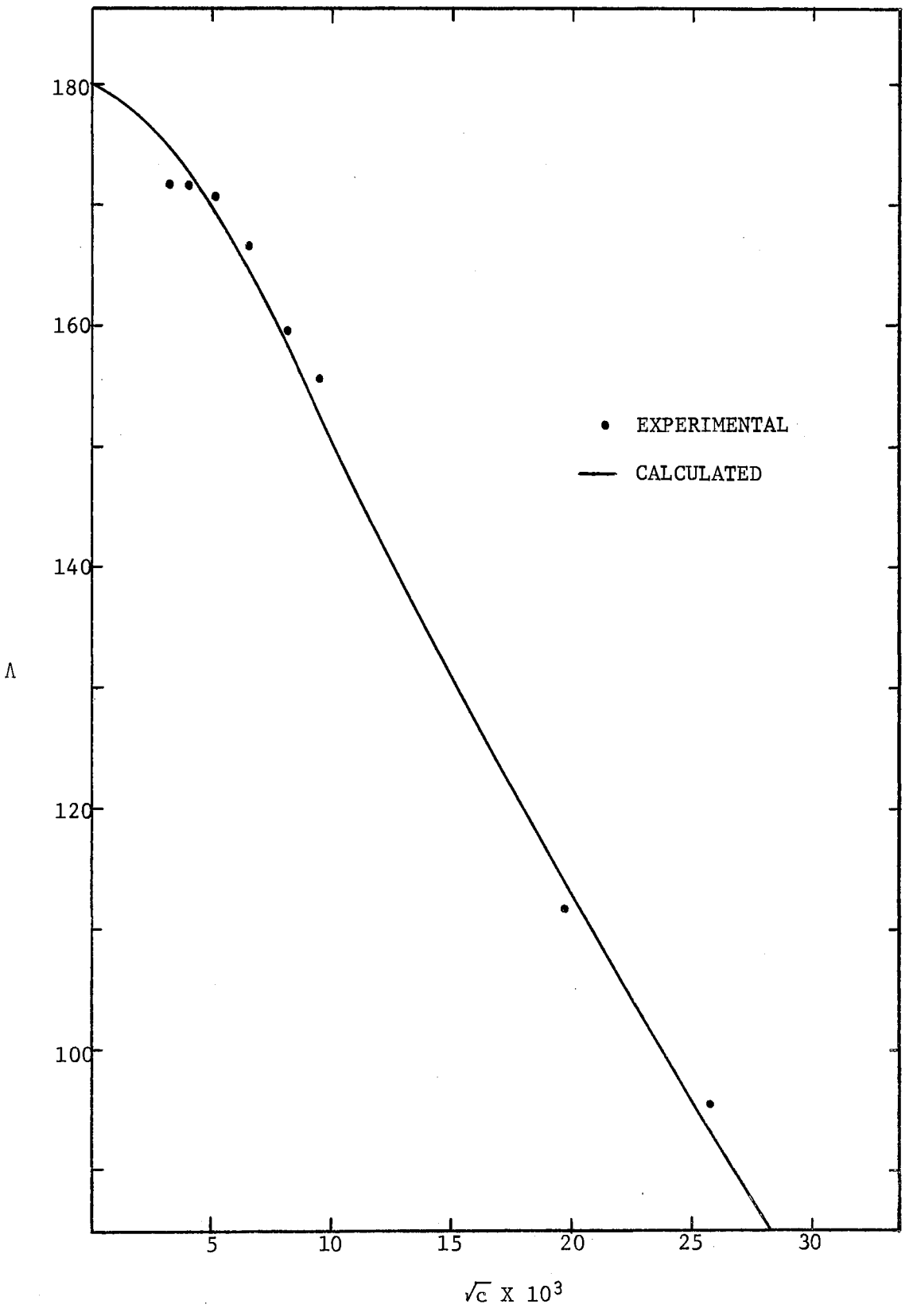

Figure 23. Phoreogram of Lithium Bromide in 0.05047 Molal Dimethyl Bromosuccinate in Acetone (Solvent V)

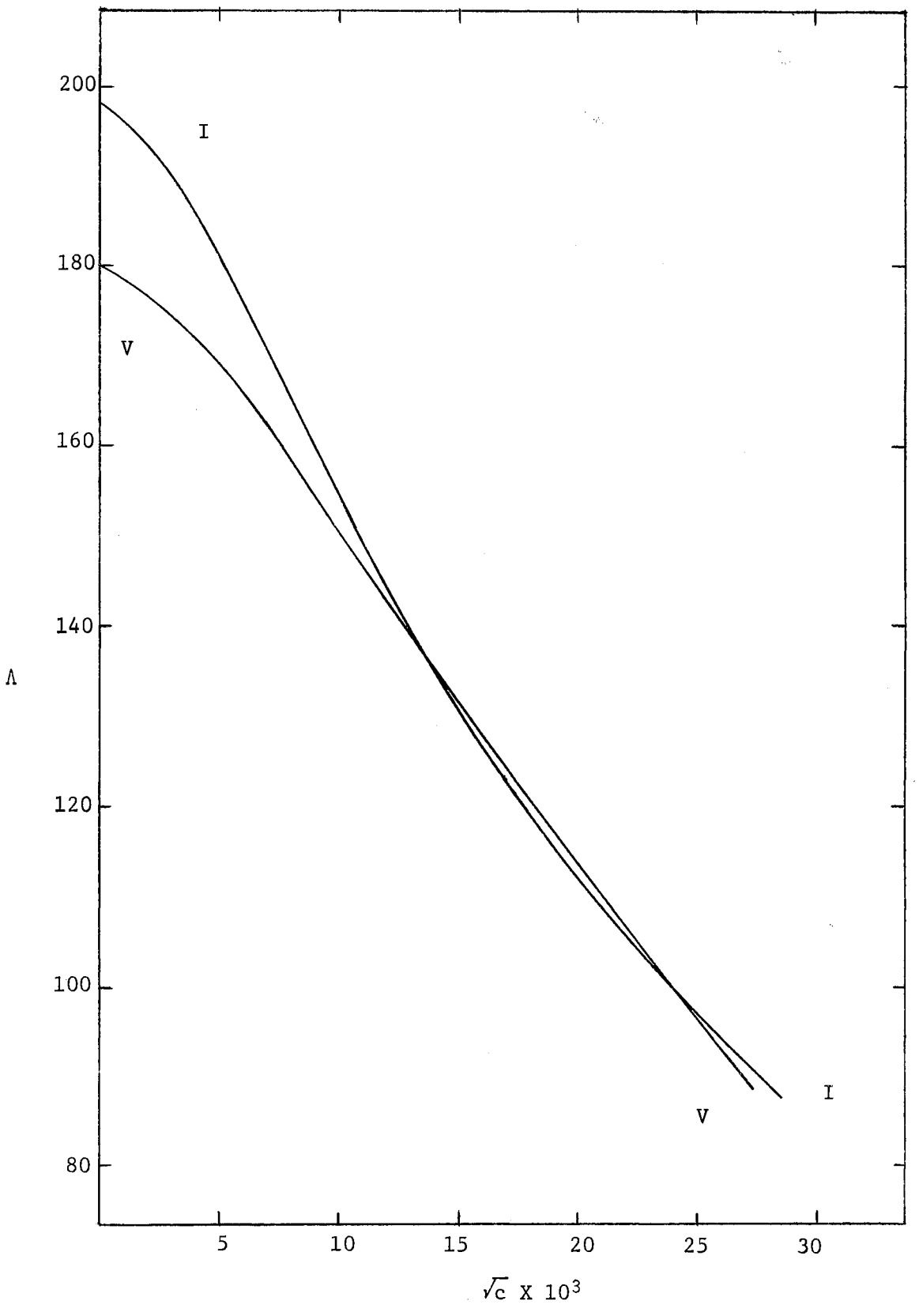

Figure 24. Lithium Bromide Phoreogram Calculated From the FOS Equation and Experimental Data for Solvents I and V

CHAPTER VII

DISCUSSION AND CONCLUSIONS

Lithium Bromide in Acetone

It can be perceived from Table III that the solvent correction for the specific conductance of lithium bromide in Series I was negligible throughout ranging from 0.025 percent for Point I10 to 0.76 percent for Point I2. (It was mentioned in Chapter II that Dutoit and Levrier (167) applied a solvent correction of 21 percent to their most dilute solution of lithium bromide in acetone. They made a correction of 5.8 percent for a 1.138×10^{-5} molar lithium bromide solution; this concentration is essentially the same as that of Point I2.) Consequently, the uncorrected specific conductance and corrected specific conductance coalesce even for Points I2-I4 as is evident from Figures 7 and 8.

The relative standard deviations of the calculated parameters (the standard deviation of the parameter divided by the value of the parameter) can be calculated from data in the first row of Table VIII; they are 0.0045, 0.49 and 0.044 for Λ_o, L and K_A, respectively. The standard deviation for L is especially large; however, this great uncertainty in L is not uncommon for smenogenic solvents. Fuoss, Onsager and Skinner (136) pointed out that "no useful information can be obtained from the ion-pair term at high dielectric constants nor from the linear term at low." They tabulated the results of analysis of data from previous work. For example, using data of Lind and Fuoss (228) (229) for

dioxane-water mixtures they computed values with a dielectric constant of 12.74 of -433±108 and 1702±32 for L and K_A, respectively, for potassium chloride and with a dielectric constant of 15.29 they obtained values of 44±85 and 313±14 for L and K_A, respectively, for cesium iodide. With data from Berns and Fuoss (230) they calculated values of 1645±1018 and 3.6±9.6 for L and K_A, respectively, for tetramethylammonium tetraphenylboride in an acetonitrile-carbon tetrachloride mixture with a dielectric constant of 36.01.

Table IX shows that γ decreases as the concentration increases, which is as expected and illustrated in Figure 14. All of the terms listed in the table diminish the equivalent conductance from Λ_o and the magnitude of the reduction for each term increases with augmentation of the concentration. The K_A term makes the largest contribution to the decrease throughout the entire concentration range and the E term the smallest. At the lower concentrations the E term and L term are of the same magnitude, but at the higher concentrations the L term is about double the E term. The S term is greater than the L term at all concentrations. The values given for $\delta\Lambda$ seem to be reasonable and the calculated and experimental values for Λ are in good agreement as is reflected in the phoreogram in Figure 19.

In order to compare the results of this research with other work the data of previous investigators of the electrolytic conductance of lithium bromide in acetone were compiled and run through the program. It should be noted in Table II that only Dutoit and Levrier (167) and Bjornson (163) collected experimental data suitable for analysis by the FOS equation and only the data of Bjornson were at 25 °C. The original data of Dutoit and Levrier are included in the paper by Kraus and Bray

(25) and of Bjornson in his thesis. In the case of Dutoit and Levrier the composition of the solutions was expressed in dilution (c^{-1}) and the equivalent conductance in Siemens' units which must be multiplied by the factor 1.069 in order to convert to Ω^{-1} cm^2 eq^{-1}. Table XIV gives the calculated parameters of the FOS equation yielded from the computer program and Bjornson's data and the converted data of Dutoit and Levrier. The values obtained for the constants for Series I (which are given in Table VIII) are also included for comparison. As in Table VIII, Table XIV lists Λ_o, L and K_A along with their standard deviations, b as calculated from K_A and Equation (6-23), and a (in Å) as computed from Equation (6-21).

TABLE XIV

CONSTANTS OF FOS EQUATION FOR LITHIUM BROMIDE CALCULATED FROM DATA OF DUTOIT AND LEVRIER, BJORNSON, AND JONES

Data Source	Λ_o	L	K_A	b	a
Dutoit and Levrier (18 °C)	165.15±1.61	-665±705	1745±75	10.65	2.54
Bjornson (25 °C)	196.92±4.17	7420±43 880	4755±782	12.01	2.25
Jones (25 °C) (Series I)	198.14±0.90	-16 905±8357	3320±145	11.53	2.35

It is evident from Table XIV that both the standard deviation and relative standard deviation for Λ_o are considerably smaller for Series I than for either Dutoit and Levrier or Bjornson. The value obtained for

Λ_o from the data of Dutoit and Levrier is in excellent agreement with the value they got from the same data (166 Ω^{-1} cm^2 eq^{-1}) and with the value obtained from the same data by Kraus and Bray (165 Ω^{-1} cm^2 eq^{-1}) using the graphical method of Equation (1-11). The value for Λ_o from Bjornson's data is also in excellent agreement with the value realized by him from the same data using the Fuoss method (196.0 Ω^{-1} cm^2 eq^{-1}).

The relative standard deviation of L is smaller for Series I than for either of the other two sets of data, but the data of Dutoit and Levrier yield the smallest absolute value for the standard deviation of L. The value obtained for L with Bjornson's data gives a positive contribution from the L term in the FOS equation whereas the other two entries in the third column of Table XIV produce a negative contribution. If, however, L is calculated from Equation (1-121) with the value procured for b from the experimental K_A and Equation (1-129), a negative value for L is obtained for all three entries.

The relative standard deviation of K_A from the data of Dutoit and Levrier is essentially the same as from Series I and several times smaller than from Bjornson's data. Kraus and Bray obtained a value of 5.7×10^{-4} for K_D using the graphical method of Equation (1-11) and the data of Dutoit and Levrier. This yields a value of 1.75×10^3 for K_A, which is in perfect agreement with the value given in Table XIV for these data. Bjornson calculated a value of 2.13×10^{-4} for K_D--equivalent to 4.69×10^3 for K_A--by the Fuoss method. This, too, is in excellent agreement with the value listed in Table XIV for his data.

Other results of the Fuoss-Onsager-Skinner theoretical treatment of the data of Dutoit and Levrier and the data of Bjornson are included in Tables XV and XVI, respectively. The first and second columns give the

TABLE XV

EXPERIMENTAL AND THEORETICAL CALCULATIONS FOR LITHIUM BROMIDE IN ACETONE FROM DATA OF DUTOIT AND LEVRIER

$c \times 10^5$	Λ (experimental)	γ	Λ (calculated)	$\delta\Lambda$
.3258	158.6	0.967	163.2	4.6
1.138	161.2	0.990	159.9	-1.3
4.149	152.9	0.951	151.4	-1.5
14.11	136.2	0.866	133.2	-3.0
46.79	107.2	0.708	106.3	-0.9
168.5	73.4	0.516	75.3	1.9
620.7	46.5	0.366	46.5	0.0
1961	29.6	0.275	29.5	-0.1

TABLE XVI

EXPERIMENTAL AND THEORETICAL CALCULATIONS FOR LITHIUM BROMIDE IN ACETONE FROM DATA OF BJORNSON

$c \times 10^5$	Λ (experimental)	γ	Λ (calculated)	$\delta\Lambda$
3.474	169.7	0.879	170.6	1.0
6.660	156.4	0.816	156.2	-0.2
9.664	147.5	0.773	145.7	-1.7
12.54	140.7	0.740	137.6	-3.1
16.51	128.9	0.680	132.1	3.2
32.37	108.9	0.581	110.5	1.6
47.77	97.68	0.525	97.41	-0.3
62.54	89.84	0.486	89.04	-0.8

experimental concentration (c) and equivalent conductance (Ω^{-1} cm^2 eq^{-1}), respectively; the calculated values for γ and Λ are listed in the third and fourth columns, respectively, and the last column gives $\delta\Lambda$--the calculated equivalent conductance minus the experimental equivalent conductance. It should be noted that the same trend is observed for γ in these tables as for γ in Series I; the values of γ for Series I are given in Table IX and displayed graphically in Figure 14.

It appears that by and large the FOS equation does satisfactorily describe the electrolytic conductance of the lithium bromide-acetone system. However, some doubt may be introduced by scrutinizing the last column of Table IX which shows that the change in sign for $\delta\Lambda$ for Series I may not be random. In particular, the most dilute solution had a positive value for $\delta\Lambda$ and its magnitude was greater than for any others in the series. In the range 5-10 x 10^{-5} molar lithium bromide, $\delta\Lambda$ was negative; it became positive as the concentration was increased further, but was negative for the most concentrated solution. This is shown in the phoreogram in Figure 19 and in itself would not be significant. The last column of Table XV shows that the same pattern exists, however, for $\delta\Lambda$ for the data of Dutoit and Levrier. In fact, Kraus and Bray rejected the point corresponding to the first row. As seen in Table XVI, Bjornson's data show a similar trend. In all cases the experimental phoreogram has a greater curvature and inflection than the calculated phoreogram. The calculated phoreogram is high for the very dilute solution, low for the more concentrated solutions and has a less negative slope at the point of inflection. This same pattern is observed for Series II-V as shown in Tables X-XIII and Figures 20-23; of course, it is realized that these systems contain another component, but

nonetheless the pattern is there. These results suggest that phenomena may be occurring which are not accounted for by the Fuoss-Onsager-Skinner theory. For example, adsorption of ions at the electrodes would introduce a larger error for the very dilute solutions.

In view of the extreme precautions (described in detail in Chapters III, IV and V) taken in the experimental portion of this work and the other factors mentioned in this section, it should be apparent that the best values available for $\underline{\Lambda_o}$ and $\underline{K_A}$ for lithium bromide in acetone at 25 °C are 198.1±0.9 Ω^{-1} cm^2 eq^{-1} and (3.3±0.1) x 10^3, respectively. It appears that this research has also yielded the best value for $\underline{a}$ for lithium bromide in acetone at 25 °C--namely, 2.35 Å.

Lithium Bromide-Bromosuccinic Acid-Acetone System

The specific conductance of bromosuccinic acid in acetone at the concentrations used in this research is about two orders of magnitude greater than that of acetone and approaches the same order of magnitude as that of the very dilute solutions of lithium bromide in acetone. A plot of the corrected specific conductance of bromosuccinic acid in acetone as a function of its concentration is shown in Figure 13 and is also represented by curves in Figures 11 and 12. These graphs are in agreement with the results of Bjornson (163) who found the specific conductance of 0.02 molal bromosuccinic acid in acetone to be about 8 x 10^{-7} Ω^{-1} cm^{-1} and of 0.2 molal bromosuccinic acid in acetone to be about 4 x 10^{-6} Ω^{-1} cm^{-1}. The solvent correction for the specific conductance of lithium bromide in the bromosuccinic acid-acetone mixed

solvent is no longer negligible throughout the entire concentration ranges. Inspection of Tables IV-VI shows that, as expected, the corrections became more significant with decreasing concentration of lithium bromide and increasing concentration of bromosuccinic acid. They extended from 0.86 percent, 1.5 percent and 2.5 percent for Points II11, III11 and IV11, respectively, to 40 percent, 62 percent and 74 percent for Points II2, III2 and IV2, respectively. The consequence of these corrections is emphasized by comparing Figures 7 and 8 which display the uncorrected and corrected specific conductance of lithium bromide for Series I-IV for very dilute solutions.

It can be observed in Figure 8 that in the dilute lithium bromide solutions the increase in specific conductance with increasing concentration of lithium bromide was diminished with augmentation of bromosuccinic acid. Figure 9 indicates this held true up to a concentration of about 2-3 x 10^{-4} molar lithium bromide whereas at concentrations greater than about 5 x 10^{-4} molar lithium bromide the specific conductance is enhanced by the addition of bromosuccinic acid. It can be deduced from the figure that the specific conductance of 10^{-3} molar lithium bromide was higher by 10 percent, 13 percent and 18 percent for solutions with bromosuccinic acid molalities of 0.02, 0.05 and 0.1, respectively. On the basis of the divergence of the curves at this concentration it is reasonable to assume that if the concentration of lithium bromide is increased the enhancement of the specific conductance from the addition of the bromosuccinic acid should be increased. This is consistent with the results of Bjornson, who measured the specific conductance of solutions containing 0.01 molal lithium bromide in ace-

tone and varying amounts of bromosuccinic acid.[1] He found the specific conductance of the solution to be 3.0×10^{-4} Ω^{-1} cm^{-1} in the absence of bromosuccinic acid; for 0.02 molal, 0.05 molal, 0.1 molal and 0.2 molal bromosuccinic acid in the solution the specific conductances were 3.4×10^{-4} Ω^{-1} cm^{-1}, 4.0×10^{-4} Ω^{-1} cm^{-1}, 4.4×10^{-4} Ω^{-1} cm^{-1} and 4.6×10^{-4} Ω^{-1} cm^{-1}, respectively, which were increases of 13 percent, 33 percent, 47 percent and 53 percent, respectively. In Chapter II it is stated that Olson and Cunningham (162) found that the addition of bromosuccinic acid to 0.01 molal lithium bromide in acetone increased the specific conductance by 30 percent when the solution was 0.2 molal with respect to the acid.

It is to be noted from Table VIII that as in Series I the standard deviation of $\underline{\Lambda_o}$ is small, that of $\underline{L}$ is large and that of $\underline{K_A}$ is intermediate for Series II-IV. These large standard deviations can be rationalized in the same manner as in the preceding section. Table VIII shows that the equivalent conductance at infinite dilution decreases with increasing bromosuccinic acid concentration; Figure 15 indicates that the decrease is systematic. The table also infers a systematic decrease in $\underline{K_A}$ as the bromosuccinic acid concentration is increased; this decrease is displayed in Figure 16. The value of $\underline{a}$ increases with increasing concentration of bromosuccinic acid and is shown in Figure 17.

Tables IX-XII show that $\underline{\gamma}$ decreases with increasing concentration of lithium bromide for each series, but that the decrease gets smaller as the bromosuccinic acid concentration gets larger. The effect of

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[1]In acetone solutions the molarity and normality of lithium bromide are approximately 80 percent of the molality.

lithium bromide and bromosuccinic acid concentration on γ is demonstrated in Figure 14. All of the terms listed in Tables X-XII diminish the equivalent conductance from Λ_o for Series II-IV, just as they do for Series I, and the magnitude of the reduction for each term gets larger with increasing lithium bromide concentration, just as it does for Series I. Examination of the E terms and L terms shows that their contributions to the equivalent conductance are comparable to Series I; that is, the E terms make the smallest contribution to the decrease throughout the entire concentration ranges and at the lower concentrations the E terms and L terms are of the same magnitude, but at the higher concentrations the L terms are two to three times the E terms. For Series II and III the K_A terms make the largest contribution to the reduction in equivalent conductance at higher concentrations, but, unlike Series I, at lower concentrations the S terms are the largest contributors. The S term makes the largest contribution to the decrease in equivalent conductance at all concentrations in Series IV. The same trends are noted in $\delta\Lambda$ for Series II-IV as in Series I, but are even more pronounced; this has already been pointed out in the preceding section. There is general agreement between the experimental and calculated equivalent conductances, but the agreement is not as good as in Series I. This can be seen by comparing the experimental and calculated phoreograms shown in Figures 19-22. The calculated phoreograms for Series I-IV are shown in Figure 18. In each series the first derivative is negative throughout and there is a point of inflection with the second derivative being negative at low concentrations and positive at high concentrations.

As stated in Chapter II, one of the two purposes of this research was to determine whether or not the electrolytic conductance of the lithium bromide-bromosuccinic acid-acetone system can be described by the FOS equation by treating the system as lithium bromide in a mixed solvent. In other words, if one took into account the changes in dielectric constant, viscosity and specific conductance of the mixed solvent due to variations of composition, would a constant value be obtained for Λ_o? Obviously, it is not--the FOS equation does not describe the system.

If the system behaves ideally with no interaction among the components the specific conductances should be additive. Figure 12 shows the specific conductance of the solution corrected for the specific conductance of the acetone and lithium bromide--that is, the specific conductance of the solution minus the specific conductance obtained in Series I--for various fixed amounts of lithium bromide as a function of bromosuccinic acid concentration. Inasmuch as this is equal to the equivalent conductance of bromosuccinic acid, if there is no interaction among the conducting species all four curves should coincide with the curve for no lithium bromide. Clearly, some type of interaction must occur.

Bjornson worked at sufficiently high concentration (0.01 molal lithium bromide) that he observed only the increase in specific conductance due to addition of bromosuccinic acid to a lithium bromide-acetone solution. Lithium bromide is an ionophore and in acetone exists as lithium ions and bromide ions (conductors) in equilibrium with associated lithium bromide ion pairs (nonconductors), while bromosuccinic acid is an ionogen which exists in acetone as bromosuccinic acid molecules

(nonconductors) in equilibrium with hydrogen ions and bromosuccinate ions (conductors). In order to explain the anomalous increase in specific conductance Bjornson proposed that when bromosuccinic acid is added to the lithium bromide-acetone solution, bromide ion from the lithium bromide combines with hydrogen ion from the bromosuccinic acid and forms molecular hydrogen bromide (a nonconductor). This would result in a decrease in ions; however, as bromide ions and bromosuccinate ions were removed less lithium bromide would be associated and more bromosuccinic acid would be dissociated. The final result after establishment of equilibrium among lithium ions, bromide ions, hydrogen ions, bromosuccinate ions, bromosuccinic acid molecules, hydrogen bromide molecules and lithium bromide ion pairs would be a net increase in conducting species and therefore an increase in specific conductance.

Bjornson also measured the specific conductance of a solution of 0.01 molal lithium bromide in acetone with various amounts of dimethyl bromosuccinate added and found a slight linear decrease in specific conductance with augmentation of dimethyl bromosuccinate. Olson and Cunningham, as stated in Chapter II, obtained like results and also found that the specific conductance decreases linearly as bromosuccinic acid is added to 0.01 molal lithium perchlorate in acetone. These results lent support to Bjornson's postulate in that when the acidic hydrogens of bromosuccinic acid were replaced with methyl groups or the bromide ions of lithium bromide were replaced with perchlorate ions an increase in specific conductance was not observed.

Series V consisted of adding lithium bromide to a fixed amount of dimethyl bromosuccinate in acetone. Table VII shows that the solvent correction is greater than for Series I, but less than for Series II-IV.

The specific conductance of lithium bromide in dimethyl bromosuccinate-acetone was slightly less than in acetone, although, as seen in Figure 10, when they are plotted together on the same axes over the entire concentration range they are essentially the same. This is in contrast to Series II-IV as can be seen in Figure 9. Table VIII shows that both $\underline{\Lambda_o}$ and $\underline{K_A}$ are less than for Series I but greater than for Series II-IV. Table XIII, which gives the functions calculated from the FOS equation for Series V, indicates that the trends in each column are the same as for Series I (Table IX). The experimental and calculated phoreograms for Series V are exhibited in Figure 23. Figure 24, which compares the calculated phoreograms for Series I and V, shows that at a lithium bromide concentration of approximately 10^{-3} molar the equivalent conductance of lithium bromide is not increased by the addition of dimethyl bromosuccinate as it is by the addition of bromosuccinic acid (Figure 18). The results of Series V are in agreement with those of Bjornson and those of Olson and Cunningham.

Bjornson's postulate seems to be a plausible explanation for the increase in specific conductance of lithium bromide in acetone, provided that in acetone the dissociation constant of bromosuccinic acid is greater than that of hydrogen bromide. (It is mentioned in Chapter II that Bailey (164) obtained a value of 1×10^{-6} for $\underline{K_D}$ for hydrogen bromide in acetone.) However, in view of the fact that at lower concentrations of lithium bromide there is an actual decrease in specific conductance upon the addition of bromosuccinic acid to the system, Bjornson's proposed explanation is invalid.

It is evident from this study that there is no simple explanation

for the observed specific conductance in the lithium bromide-bromosuccinic acid-acetone system. If Table VIII is compared with Table I, which has tabulations of the effect of addition of water to the lithium bromide-acetone system (from Olson and Konecny (170)) it is noted that there is a close parallel. There are decreases in $\underline{\Lambda_o}$ and $\underline{K_A}$ ($\underline{K_A}$ and $\underline{K_D}$ being reciprocals of one another) and an increase in $\underline{a}$ in both instances. Indeed, the decrease in $\underline{\Lambda_o}$ shown in Table VIII and Figure 15 could be partially rationalized by the increase in $\underline{a}$ noted in Table VIII and displayed in Figure 17. The value obtained for $\underline{a}$ in Series I is in good agreement with that obtained from Olson and Konecny. If the increase in $\underline{a}$ is a result of increased solvation of the ions, then one might expect the mobility of the ions to be decreased and consequently the equivalent conductance at infiniate dilution to be reduced. Also, an increase in viscosity should decrease the mobility; however, the increase in viscosity due to the addition of bromosuccinic acid is negligible. Finally, it should be noted that Walden's rule--Equation (1-13)--does not apply; the product, $\underline{\Lambda_o \eta}$, decreases with increasing concentration of bromosuccinic acid.

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APPENDIX A

FUNDAMENTAL AND DEFINED UNITS, PHYSICAL CONSTANTS, AND FORMULA MASSES

TABLE XVII

NAMES, SYMBOLS AND DEFINITIONS OF BASIC SI UNITS

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length: meter; m; the length equal to 1 650 763.73 (exactly) wavelengths in a vacuum of the radiation corresponding to the transition between the energy levels $2p_{10}$ and $5d_5$ of the pure nuclide ^{86}Kr.

mass: kilogram; kg; the mass of the International Prototype Kilogram which is in the custody of the Bureau International des Poids et Measures at Sévres, France.

time: second; s; the duration of 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels (F=4, M_F=0 and F=3, M_F=0) of the fundamental state (2S 1/2) of the atom of cesium 133.

electric current: ampere: A; that constant current which, if maintained in two parallel rectilinear conductors, of infinite length and of negligible circular cross-section, at a distance apart of one meter in a vacuum, would produce a force between the conductors equal to 2×10^{-7} newton per meter of length.

thermodynamic temperature: kelvin, K; the unit of thermodynamic temperature which is the fraction 1/273.16 exactly of the thermodynamic temperature at the triple point of water.

amount of substance: mole; mol; the amount of substance of a system which contains as many elementary units as there are carbon atoms in 0.012 kg (exactly) of the pure nuclide ^{12}C.

Source: Information Bulletin No. 32, I.U.P.A.C., August (1968).

TABLE XVIII

NAMES, SYMBOLS AND DEFINITIONS
OF DERIVED SI UNITS

Physical Quantity	Name	Symbol	Definition
electric capacitance	farad	F	$A^2\ s^4\ kg^{-1}\ m^{-2}$ (A s V^{-1})
electric charge	coulomb	C	A s
electric potential difference	volt	V	kg $m^2\ s^{-3}\ A^{-1}$ (J $A^{-1}\ s^{-1}$)
electric resistance	ohm	Ω	kg $m^2\ s^{-3}\ A^{-2}$ (V A^{-1})
energy	joule	J	kg $m^2\ s^{-2}$
force	newton	N	kg m s^{-2}
frequency	hertz	Hz	s^{-1}
power	watt	W	kg $m^2\ s^{-3}$ (J S^{-1})

Source: Information Bulletin No. 32, I.U.P.A.C., August (1968).

TABLE XIX

NAMES, SYMBOLS AND DEFINITIONS OF OTHER UNITS

Physical Quantity	Name	Symbol	Definition
amount of substance	equivalent	eq	mol Z^{-1}
concentration	demal	D	eq(solute) dm^{-3}(solution)
concentration	molal	m	mol(solute) kg^{-1}(solvent)
concentration	molar	M	mol(solute) dm^{-3}(solution)
concentration	normal	N	eq(solute) dm^{-3}(solution)
customary temperature (t)	Celsius degree	°C	t/°C = T/K - 273.15
dynamic viscosity	poise	P	10^{-1} kg m^{-1} s^{-1}
electric charge	electrostatic unit	esu	3.33560×10^{-10} C
energy	erg	erg	10^{-7} J
force	dyne	dyn	10^{-5} N
length	angstrom	Å	10^{-10} m
length	inch	in	2.54×10^{-2} m
pressure	torr	Torr	(101 325)/760 N m^{-2}
volume	liter	ℓ	10^{-3} m^3
volume	ounce	oz	2.95737×10^{-5} m^3

Source: Information Bulletin No. 32, I.U.P.A.C., August (1968).

TABLE XX

NUMERICAL VALUES OF FUNDAMENTAL CONSTANTS

Quantity	Symbol	Value
Avogadro constant	N	$(6.02252 \pm 0.00028) \times 10^{23}$ mol^{-1}
Boltzmann constant	k	$(1.38054 \pm 0.00009) \times 10^{-23}$ J K^{-1}
charge of proton	ε	$(1.60210 \pm 0.00007) \times 10^{-19}$ C
Faraday constant	F	$(9.64870 \pm 0.00016) \times 10^{4}$ C mol^{-1}
gas constant	R	(8.31433 ± 0.00044) J K^{-1} mol^{-1}
speed of light in vacuum	C	$(2.997925 \pm 0.000003) \times 10^{8}$ m s^{-1}
	e	2.71828
	π	3.14159
	Γ	0.577216

Source: Information Bulletin No. 32, I.U.P.A.C., August (1968).

TABLE XXI

FORMULA MASSES OF COMPOUNDS

Compound	Formula Weight (g mol^{-1})
acetone	58.08
bromosuccinic acid	197.0
dimethyl bromosuccinate	225.0
lithium bromide	86.85
potassium chloride	74.56

Source: Handbook of Chemistry and Physics (Weast, R. C., ed.), 51st edition, The Chemical Rubber., Cleveland, Ohio, 1970.

APPENDIX B

ABSTRACTS FROM THE FIRST FOUR PAPERS BY FUOSS AND ONSAGER ON THE CONDUCTANCE OF SYMMETRICAL ELECTROLYTES

I. Potential of Total Force (131)

By means of a multiplicative expansion of the distribution functions which describe local ionic concentrations, the 1932 Onsager-Fuoss equation of continuity can be integrated with explicit retention of the Boltzmann factor, instead of approximating the latter by a truncated power series. The result is expressed in terms of the potential $\underline{\mu_{jj}}$ of total force acting on a given ion: the present approximation to $\underline{\nabla\mu_{jj}}$ includes the external field, the forces due to neighboring ions and to the asymmetry of the ionic atmospheres, and the virtual forces due to local concentration gradients. The differential equations which will lead to the forces from the velocity field also have been derived.

II. The Relaxation Field (132)

The Poisson equation for the asymmetry potentials of a symmetrical electrolyte in the conductance process has been integrated by the use of the corresponding Green's function in order to obtain the purely electrostatic terms of the relaxation field. The Boltzmann factor in the distribution function was retained explicitly as an exponential throughout the calculation, instead of approximating it as a truncated series as has been customary in previous derivations. The consequence of this refinement in mathematical methods is the appearance in the relaxation field of a term which will lead to a decrease in conductance with increasing concentration or decreasing dielectric constant. The decrease is proportional to the product of concentration and the square of the mean activity coefficient. It depends on dielectric constant through a function which has as its asymptotic limit $\underline{e}\underline{b}/\underline{b}^3$ ($\underline{b}=\underline{\epsilon}^2/\underline{aDkT}$), which is the form of the

theoretical association constant for contact pairs. This result means that the ad hoc hypothesis of ion pairing controlled by a mass action equilibrium is no longer needed to obtain a satisfactory conductance function; the former mass action term is derivable from the Poisson equation. It was missed in earlier theoretical work by too drastic approximation of the Boltzmann factor.

III. Electrophoresis (133)

The electrophoretic velocity in a dilute solution of a symmetrical electrolyte has been computed, with the following improvements over earlier treatments of the problem: (1) the volume force is calculated as the gradient of the potential of the total force acting on an ion instead of being approximated merely by the force due to the external field; (2) the Boltzmann factor is retained explicitly, instead of being approximated by a truncated series; and (3) the Oseen equations of motion (rather than the Stokes) are used. The result gives the Onsager 1926 limiting value ($-\varepsilon_j \kappa X/6\pi\eta$) as the leading term; to next approximation, this is opposed by a term proportional to concentration, which depends on $b=\varepsilon^2/aDkT$ in a non-exponential fashion. For example, for $b=1.5$ ($D\simeq 100$), $F(b)=2.31$ and for $b=15$ ($D\simeq 10$), $F(b)=-0.77$. The coefficient goes through zero near $b=5$.

IV. Hydrodynamic and Osmotic Terms in the Relaxation Field (134)

Using (1) the differential equation which defines that part of the total potential which has hydrodynamic origin, (2) the corresponding Poisson equation, and (3) the appropriate boundary conditions, the term ΔX_v in the relaxation field is calculated up to terms of order $c^{1/2}$ in concentration in the conductance function $\Lambda(c)$. The Boltzmann factor e^{ζ} is kept explicit as $\exp(-\beta e^{-\kappa r}/r)$ throughout the computation; the principal approximations made are to drop terms of order $\kappa^3 \sim c^{3/2}$. The leading term contains the negative exponential integrals $E_n(2\kappa a)$ and $E_n(\kappa a)$ and thus contributes $c\log c$ terms to $\Lambda(c)$; these are identical with our previous result. The next term, linear in c, has a coefficient $[E_n(b)/2-(2b)^{-1}\exp(b)(1-1/3b)]$, $b=\varepsilon^2/aDkT$, which contains most of the function $K(b)$ which appeared in the electrostatic part $[\Delta X]$ of the relaxation field. The kinetic term in $\Lambda(c)$ is also computed to the same degree of approximation; combined with $[\Delta X]$, it gives the complete function $K(b)$, multiplied by a small coefficient.

APPENDIX C

COMPUTER PROGRAM LISTING FOR CONCENTRATION CALCULATIONS

```
     000000000111111111122222222223333333333444444444455555555556666666666777777777 8
     123456789012345678901234567890123456789012345678901234567890123456789012345678 90
CARD
   1 C*************************************************************************
   2 C******************************  PROGRAM TITLE  ****************************
   3 C            CALCULATION OF CONCENTRATIONS FOR USE WITH DILUTION CELLS
   4 C*************************************************************************
   5 C***************************  INPUT INSTRUCTIONS  ****************************
   6 C  THE FIRST DATA CARD REQUIRES A FORMAT (3F10.0, 3E15.4, I5).
   7 C       THE FIRST FIELD (F10.0) GIVES THE NUMBER OF GRAMS OF SOLVENT ORIGINALLY
   8 C       IN THE CELL.
   9 C       THE SECOND FIELD (F10.0) GIVES THE FORMULA WEIGHT OF THE SOLUTE.
  10 C       THE THIRD FIELD (F10.0) GIVES THE DENSITY (G/ML) OF THE SOLVENT.
  11 C       THE FOURTH FIELD (E15.4) GIVES THE NUMBER OF GRAMS OF SOLUTE PER GRAM OF
  12 C       CONCENTRATED STOCK SOLUTION (SOLUTION NO. 1).
  13 C       THE FIFTH FIELD (E15.4) GIVES THE NUMBER OF GRAMS OF SOLUTE PER GRAM OF
  14 C       INTERMEDIATE STOCK SOLUTION (SOLUTION NO. 2).
  15 C       THE SIXTH FIELD (E15.4) GIVES THE NUMBER OF GRAMS OF SOLUTE PER GRAM OF
  16 C       DILUTE STOCK SOLUTION (SOLUTION NO. 3).
  17 C       THE SEVENTH FIELD (I5) GIVES THE NUMBER OF DATA POINTS.
  18 C  THE REMAINING DATA CARDS REQUIRE A FORMAT (F10.0, I5).  EACH CARD REFERS TO
  19 C  ONE MEASURED CONCENTRATION.  THESE CARDS SHOULD BE ARRANGED IN ORDER OF
  20 C  INCREASING CONCENTRATION.
  21 C       THE FIRST FIELD (F10.0) GIVES THE NUMBER OF GRAMS OF STOCK SOLUTION
  22 C       ADDED.
  23 C       THE SECOND FIELD (I5) GIVES THE NUMBER OF THE STOCK SOLUTION ADDED
  24 C       ('1' FOR THE MOST CONCENTRATED, '2' FOR THE INTERMEDIATE, AND '3' FOR
  25 C       THE DILUTE).
  26 C  STATEMENT NUMBER 10000 IS CALLED THE COMMENT FORMAT--IT IS THE LAST FORMAT
  27 C  LISTED AND IS SEPARATED FROM THE OTHER FORMAT STATEMENTS.  ANY COMMENTS
  28 C  CONCERNING THE DATA MAY BE INSERTED HERE AND THEY WILL BE PRINTED AT THE
  29 C  BEGINNING OF THE OUTPUT.  THIS STATEMENT SHOULD BE WRITTEN AS FOLLOWS.
  30 C            10000 FORMAT (10X, 'COMMENT IN HERE.' /////)
  31 C*************************************************************************
  32 C*********************************  OUTPUT  ********************************
  33 C  THE OUTPUT CONSISTS OF THE POINT NUMBER AND CORRESPONDING LITHIUM BROMIDE
  34 C  NORMALITY AND MOLALITY.
  35 C*************************************************************************
  36 C***************************  EXPLICIT STATEMENT  ****************************
  37       REAL  LIBR, LIBRAD, MOLAL, NORMAL
  38 C*************************************************************************
  39 C***************************  FORMAT STATEMENTS  *****************************
  40      1 FORMAT (3F10.0, 3E15.4, I5)
  41      3 FORMAT (F10.0, I5)
  42      8 FORMAT (I13, 1PE21.3, E19.3 /)
  43      9OFORMAT (10X, 'POINT', 10X, 'NORMALITY', 10X, 'MOLALITY'/// 12X, '1
  44       1', 12X, '----------' 10X, '----------'/)
  45     10 FORMAT ('1')
  46 C*************************************************************************
  47 C***************************  COMMENT FORMAT  ********************************
  48 10000 FORMAT (10X, 'FAP' /////)
  49 C*************************************************************************
  50 C*********************************  PROGRAM  *******************************
  51       LIBR = 0.
  52       WRITE (6,10)
  53       WRITE (6,10000)
  54       WRITE (6,9)
```

```
     00000000011111111112222222223333333333444444444455555555556666666666777777777 8
     12345678901234567890123456789012345678901234567890123456789012345678901234567890
CARD
   55        READ (5,1) SOLVNT, GFW, DENSTY, SOLN1, SOLN2, SOLN3, KOUNT
   56        DO 2  I=1,KOUNT
   57        J = I + 1
   58        READ (5,3) ADDSOL, NUMBER
   59        GO TO (4,5,6), NUMBER
   60      4 LIBRAD = SOLN1 * ADDSOL
   61        GO TO 7
   62      5 LIBRAD = SOLN2 * ADDSOL
   63        GO TO 7
   64      6 LIBRAD = SOLN3 * ADDSOL
   65      7 LIBR = LIBR + LIBRAD
   66        SOLVNT = SOLVNT + ADDSOL - LIBRAD
   67        FORWT = LIBR / GFW
   68        MOLAL = FORWT / SOLVNT * 1000.
   69        NORMAL = FORWT * DENSTY/SOLVNT * 1000.
   70      2 WRITE (6,8) J, NORMAL, MOLAL
   71        WRITE (6,10)
   72        STOP
   73        END
   74  C*************************************************************************************
   75  C*********************************  DATA CARDS  **************************************
   76  C*************************************************************************************
```

APPENDIX D

COMPUTER PROGRAM LISTING FOR SOLUTION OF

FUOSS-ONSAGER-SKINNER EQUATION

```
     000000000111111111122222222223333333333444444444455555555556666666666777777777 8
     123456789012345678901234567890123456789012345678901234567890123456789012345678 90
CARD
   1 C*************************************************************************
   2 C*******************************  PROGRAM TITLE  *********************************
   3 C                    SOLUTION OF FUOSS-ONSAGER-SKINNER EQUATION
   4 C*************************************************************************
   5 C*****************************  INPUT INSTRUCTIONS  ******************************
   6 C  THE FIRST RECORD REQUIRES A FORMAT (12X,15A4/6X,16A4/6X,16A4), WHICH IS THE
   7 C  IDENTIFICATION FOR THE SERIES.
   8 C  THE SECOND DATA CARD REQUIRES A FORMAT (I5,4F10.0,E10.3).
   9 C       THE FIRST FIELD (I5) GIVES THE NUMBER OF POINTS IN THE SERIES.
  10 C       THE SECOND FIELD (F10.0) GIVES THE CELL CONSTANT.
  11 C       THE THIRD FIELD (F10.0) GIVES THE ABSOLUTE TEMPERATURE.
  12 C       THE FOURTH FIELD (F10.0) GIVES THE VISCOSITY.
  13 C       THE FIFTH FIELD (F10.0) GIVES THE DIELECTRIC CONSTANT.
  14 C       THE SIXTH FIELD (E10.3) GIVES THE SPECIFIC CONDUCTANCE OF THE SOLVENT.
  15 C  THE REMAINING DATA CARDS FOR THE SERIES REQUIRE (E12.3,10X,E12.5,10X,E12.5)
  16 C  FORMATS.  EACH CARD REFERS TO A PAIR OF MEASUREMENTS--CONCENTRATION AND
  17 C  CORRESPONDING RESISTANCE.  THESE CARDS SHOULD BE ARRANGED IN ORDER OF
  18 C  INCREASING CONCENTRATION.
  19 C       THE FIRST FIELD (E12.3E GIVES THE SOLUTE CONCENTRATION (MOLES/LITER).
  20 C       THE SECOND FIELD (E12.5) GIVES THE MEASURED RESISTANCE (OHMS).
  21 C       THE THIRD FIELD (E12.5) GIVES THE RESISTANCE (OHMS) OF THE SHUNT.
  22 C  THESE CARDS COMPLETE THE SET FOR ONE SERIES.  IF MORE THAN ONE SERIES IS RUN,
  23 C  THE ABOVE SEQUENCE OF CARDS IS REPEATED FOR EACH SERIES AND PLACED ONE AFTER
  24 C  ANOTHER.
  25 C
  26 C  IN ADDITION, THE FOLLOWING SHOULD BE CHECKED.
  27 C       THE TEST VALUE ON CARD 0145 GIVES THE NUMBER OF SERIES BEING DETERMINED.
  28 C       THE TRIAL VALUE FOR B IS GIVEN BY CARD 0201.
  29 C       THE TRIAL VALUE FOR K IS GIVEN BY CARD 0225.
  30 C*************************************************************************
  31 C*********************************  OUTPUT  ***********************************
  32 C  THE OUTPUT CONSISTS OF SERIES IDENTIFICATION, TEMPERATURE, CELL CONSTANT,
  33 C  VISCOSITY, DIELECTRIC CONSTANT, SOLVENT SPECIFIC CONDUCTANCE, E1, E2, ALPHA
  34 C  AND BETA.  THIS IS FOLLOWED BY THE CONCENTRATION, SQUARE ROOT OF THE
  35 C  CONCENTRATION, RESISTANCE, SPECIFIC CONDUCTANCE (CORRECTED) AND EQUIVALENT
  36 C  CONDUCTANCE FOR EACH POINT.  THE FIRST ESTIMATE OF THE EQUIVALENT CONDUCTANCE
  37 C  AT INFINITE DILUTION, THE ZEROTH AND FIRST APPROXIMATION OF GAMMA FOR EACH
  38 C  POINT, THE INITIAL VALUE OF B AND THE ESTIMATE OF L OBTAINED FROM IT AND THE
  39 C  REFINED APPROXIMATIONS OF GAMMA FOR EACH POINT ARE GIVEN.  EACH TIME THE
  40 C  LEAST SQUARES SUBROUTINE IS CALLED, THE ELEMENTS OF THE NORMAL AND INVERSE
  41 C  MATRICES ARE LISTED ALONG WITH VALUES FOR LAMBDA ZERO, K, AND L AND THEIR
  42 C  STANDARD DEVIATIONS PLUS VALUES FOR B, A AND THE VALUE OF L CALCULATED FROM
  43 C  THE VALUE OBTAINED FOR B.  ALSO, ON EACH PASS OF THE SUBROUTINE VALUES OF THE
  44 C  FOLLOWING ARE TABULATED FOR EACH POINT.
  45 C       MOLAR CONCENTRATION
  46 C       GAMMA
  47 C       PRODUCT OF CONCENTRATION AND GAMMA (C*GAMMA)
  48 C       EXPERIMENTAL EQUIVALENT CONDUCTANCE
  49 C       CALCULATED EQUIVALENT CONDUCTANCE
  50 C       DELTA LAMBDA
  51 C       CONDITION EQUATION  (F0)
  52 C       PARTIAL DERIVATIVE OF CONDITION EQUATION WITH RESPECT TO LAMBDA ZERO
  53 C            (F1)
  54 C       PARTIAL DERIVATIVE OF CONDITION EQUATION WITH RESPECT TO K  (F2)
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CARD
  55 C        PARTIAL DERIVATIVE OF CONDITION EQUATION WITH RESPECT TO L  (F3)
  56 C        PARTIAL DERIVATIVE OF CONDITION EQUATION WITH RESPECT TO (C*GAMMA)  (FX)
  57 C        PARTIAL DERIVATIVE OF CONDITION EQUATION WITH RESPECT TO LAMBDA  (FY)
  58 C        EQUATION (6-13)  (L)
  59 C        SQUARE OF CONDITION EQUATION DIVIDED BY EQUATION (6-13)  (F0*F0/L)
  60 C        S TERM
  61 C        E TERM
  62 C        L TERM
  63 C        K TERM
  64 C        STANDARD DEVIATION OF (C*GAMMA)
  65 C        STANDARD DEVIATION OF LAMBDA
  66 C  FINALLY, THE RATIO OF THE MAXIMUM DEVIATION TO THE AVERAGE DEVIATION IS
  67 C  PRINTED, FOLLOWED BY INTEGRAL VALUES OF B FROM 1 TO 25 AND THE CORRESPONDING
  68 C  VALUES OF L CALCULATED FROM THEM.
  69 C*****************************************************************************
  70 C*****************************  DIMENSION STATEMENT  *****************************
  71       DIMENSION  CONCEN(20),EQUCON(20),RESIST(20),ROOTCN(20),F1000(47),
  72      1SPECON(20), GAMMA1(20), GAMMA2(20), DENOM(20), SHUNT(20),F(7,20),
  73      2VAR(20),X(20),Y(20),CONST(3),SIGY(20),SIGX(20),YCALX(20),SIG(3),
  74      3GAMMA3(20)
  75 C*****************************************************************************
  76 C*****************************  FORMAT STATEMENTS  *****************************
  77     1 FORMAT (I5, 4F10.0, E10.3)
  78     20FORMAT (10X, 'THE FOLLOWING DATA WERE OBTAINED AT', F7.2, ' KELVIN
  79      1 IN A CELL WITH A CELL CONSTANT OF', F9.6, ' /CM.' // 10X, 'THE VI
  80      2SCOSITY OF THE SOLVENT IS',  1PE10.3, ' POISE (GM/(CM*SEC)).', //1
  81      30X, 'THE DIELECTRIC CONSTANT OF THE SOLVENT IS',  0PF6.2, '.' /)
  82     4 FORMAT(E12.3,10X,E12.5,10X,E12.5)
  83     5 FORMAT (I13, 1X, 1P2E18.3, E13.5, E19.4, E26.3/)
  84     60FORMAT(//10X,'THE FIRST ESTIMATE FOR THE EQUIVALENT CONDUCTANCE AT
  85      1 INFINITE DILUTION IS', 1PE10.3, ' MHO*CM*CM/EQUIV.' / 10X, 'THIS
  86      2IS OBTAINED BY APPLYING A LINEAR LEAST SQUARES TO THE FIRST FOUR C
  87      3ONCENTRATIONS AND EQUIVALENT CONDUCTANCES ABOVE.' ///// 10X,    'A
  88      4 ZEROTH APPROXIMATION OF GAMMA IS GIVEN AS THE EQUIVALENT CONDUCTA
  89      5NCE DIVIDED BY THE FIRST ESTIMATE FOR THE EQUIVALENT' / 10X, 'COND
  90      6UCTANCE AT INFINITE DILUTION.  A FIRST APPROXIMATION IS OBTAINED B
  91      7Y DIVIDING THE EQUIVALENT CONDUCTANCE BY THE SUM OF' / 10X, 'THE F
  92      8IRST TWO TERMS OF THE FUOSS-ONSAGER EQUATION USING THE FIRST ESTIM
  93      9ATE FOR THE EQUIVALENT CONDUCTANCE AND THE ZEROTH' / 10X, 'APPROXI
  94      1MATION OF GAMMA.' /// 20X, 'NUMBER', 10X, 'GAMMA-ZERO', 10X, 'GAMM
  95      2A-ONE' /)
  96     7 FORMAT(1H1)
  97     12 FORMAT (I24, 11X, F9.5, 11X, 'INFINITE')
  98     13 FORMAT (I24, 11X, F9.5, 11X, F9.5)
  99     150FORMAT (///// 10X, 'THE PROGRAM HAS BEEN TERMINATED BECAUSE AT LEA
 100      1ST ONE VALUE OF GAMMA-ONE IS NEGATIVE OR INFINITE.' / '1')
 101     160FORMAT (///10X, 'AN ESTIMATE OF L IS OBTAINED FROM ASSUMING AN INI
 102      1TIAL VALUE OF B =', F6.2, '.  THE ESTIMATE IS ', 1PE10.3, '.'
 103      2                          //10X,        'A REFINED APPROXIMATION OF
 104      4GAMMA IS OBTAINED BY DIVIDING THE EQUIVALENT CONDUCTANCE BY THE SU
 105      5M OF THE FIRST FOUR TERMS OF' / 10X, 'THE FUOSS-ONSAGER EQUATION J
 106      6SING THE PREVIOUS ESTIMATE OF GAMMA.  THIS PROCESS IS ITERATED UNT
 107      7IL SUCCESSIVE ESTIMATES' / 10X, 'DIFFER BY LESS THAN 0.00005.' ///
 108      820X, 'NUMBER', 10X, 'GAMMA', 16X, 'SUBSCRIPT FOR GAMMA' /)
 109     20 FORMAT (I24, 11X, F7.5, 16X, 'GREATER THAN 50')
 110     22 FORMAT (I24, 11X, F7.5, I20)
 111     240FORMAT (///// 10X, 'THE PROGRAM HAS BEEN TERMINATED BECAUSE AT LEA
 112      1ST ONE VALUE OF GAMMA DOES NOT CONVERGE TO WITHIN 0.00005 IN 50 IT
 113      2ERATIONS.' / '1')
 114     290FORMAT (/10X,'THE SPECIFIC CONDUCTANCE OF THE SOLVENT IS',1PE10.3,
 115      1' MHO/CM.')
 116     310FORMAT (/10X,'THE SPECIFIC CONDUCTANCE OF THE SOLVENT IS ASSUMED T
 117      1O BE NEGLIGIBLE.')
 118     320FORMAT  (/10X, 'ALPHA =', 1PE10.3, 20X, 'BETA =', E10.3 ////
 119      1/ 10X, 'NUMBER', 5X, 'CONCENTRATION', 5X, 'SQUARE ROOT OF', 5X, 'R
 120      2ESISTANCE', 5X, 'SPECIFIC CONDUCTANCE', 5X, 'EQUIVALENT CONDUCTANC
 121      3E' / 21X, '(MOLES/LITER)', 5X, 'CONCENTRATION', 8X, '(OHMS)', 13X
 122      4, '(MHO/CM)', 13X, '(MHO*CM*CM/EQUIV)' //)
 123    100 FORMAT(12X,15A4/6X,16A4/6X,16A4)
 124    101 FORMAT(5X,' CONCEN ELCT  GAMMA  GAMMA*CONC  LAMB EXP  LAMB CAL  DE
 125      1LTA'/)
 126    102 FORMAT(5X,E12.4,F7.4,E12.4,2F10.3,F7.3)
 127    103 FORMAT(//5X,'    LAMBDA ZERO   CONSTANT K   CONSTANT L   SUM OF SQ
 128      1R')
 129    104 FORMAT(9X,F11.3,1P3E13.4)
 130    105 FORMAT(5X,'STD=',F11.3,3E13.4)
 131    106 FORMAT(/10X,'E1PRIME=',F10.4)
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      1234567890123456789012345678901234567890123456789012345678901234567890123456789 0
CARD
  132    107 FORMAT(/10X,'E2PRIME=',F10.3)
  133    108 FORMAT(//5X,'      CONSTANT B   CONSTANT A   CAL CONS L')
  134    201 FORMAT(5X,/' POINT X(',E12.5,'), Y(',E12.5,') HAS A DEVIATION OF',
  135       1F6.2,' TIMES THE STANDARD DEVIATION AND IS REJECTED'/)
  136    202 FORMAT(5X,'THE PARAMETERS INCLUDING THIS POINT ARE:',5E15.5)
  137    203 FORMAT(5X,'   THE DEVIATIONS OF THE PARAMETERS ARE:',5E15.3)
  138    204 FORMAT(11X,'THE EXTERNAL STANDARD DEVIATION IS',F9.3)
  139    205 FORMAT(//7X,'DEV EXT=',F6.2)
  140    206 FORMAT(//7X,9HDEV MAX =,F6.2,14H TIMES AVE DEV////)
  141   C*****************************************************************************
  142   C*********************************  PROGRAM  *********************************
  143         NROW=3
  144         NCOL=NROW+1
  145         DO 47 MO=1,5                                                  CHECK 1
  146         JONES=0
  147         READ(5,100)(F1000(I),I=1,47)
  148         WRITE(6,F1000)
  149         KICKER=0
  150         SUMX1=0.
  151         SUMX2=0.
  152         SUMY=0.
  153         SUMX1Y=0.
  154         READ (5,1) NUMBER, CELCON, TKELVN, VISCOS, DIELCT, SOLVSC
  155         ALPHA = .820457E+06 / (DIELCT * TKELVN)**1.5
  156         BETA = 82.4866/ VISCOS / SQRT(DIELCT * TKELVN)
  157         E1PRIM = 2.94255E+12/(DIELCT * TKELVN)**3
  158         E2PRIM = .433244E+08/VISCOS / (DIELCT * TKELVN)**2
  159         WRITE (6,2) TKELVN, CELCON, VISCOS, DIELCT
  160         WRITE(6,106)E1PRIM
  161         WRITE(6,107)E2PRIM
  162         IF (SOLVSC.EQ.0.) GO TO 28
  163         WRITE (6,29) SOLVSC
  164         GO TO 30
  165      28 WRITE (6,31)
  166      30 WRITE (6,32) ALPHA, BETA
  167         DO 3  NUMBR = 1, NUMBER
  168         READ (5,4) CONCEN(NUMBR), RESIST(NUMBR), SHUNT(NUMBR)
  169        3IF (SHUNT(NUMBR).NE.0.) RESIST(NUMBR)=SHUNT(NUMBR)*RESIST(NUMBR)/
  170        1(SHUNT(NUMBR)-RESIST(NUMBR))
  171         ROOTCN(NUMBR) = SQRT(CONCEN(NUMBR))
  172         SPECON(NUMBR) = CELCON / RESIST(NUMBR) - SOLVSC
  173         EQUCON(NUMBR) = 1000. * SPECON(NUMBR) / CONCEN(NUMBR)
  174         IF (NUMBR.GT.4) GO TO 3
  175         SUMX1 = SUMX1 + ROOTCN(NUMBR)
  176         SUMX2 = SUMX2 + CONCEN(NUMBR)
  177         SUMY = SUMY + EQUCON(NUMBR)
  178         SUMX1Y = SUMX1Y + ROOTCN(NUMBR) * EQUCON(NUMBR)
  179       3 0WRITE (6,5) NUMBR, CONCEN(NUMBR), ROOTCN(NUMBR), RESIST(NUMBR),
  180        1SPECON(NUMBR), EQUCON(NUMBR)
  181         EZERO1=(SUMX1Y*SUMX1-SUMY*SUMX2)/(SUMX1*SUMX1-4.*SUMX2)
  182         ONSAG1 = ALPHA * EZERO1 + BETA
  183         WRITE(6,F1000)
  184         WRITE (6,6) EZERO1
  185         DO 8  NMBR = 1, NUMBER
  186         GAMMA1(NMBR) = EQUCON(NMBR) / EZERO1
  187         DENOM(NMBR) = EZERO1 - ONSAG1 * ROOTCN(NMBR) * SQRT(GAMMA1(NMBR))
  188         IF (DENOM(NMBR)) 9, 10, 11
  189      10 KICKER = 1
  190         WRITE (6,12) NMBR, GAMMA1(NMBR)
  191         GO TO 8
  192       9 KICKER = 1
  193      11 GAMMA2(NMBR) = EQUCON(NMBR) / DENOM(NMBR)
  194         WRITE (6,13) NMBR, GAMMA1(NMBR), GAMMA2(NMBR)
  195       8 CONTINUE
  196         IF (KICKER.NE.1) GO TO 14
  197         WRITE (6,15)
  198         CALL EXIT
  199      14 CONTINUE
  200         E = 2.30259* (E1PRIM * EZERO1 - E2PRIM)
  201         B=10.                                                         CHECK 2
  202         GUESSL=2.*E1PRIM*EZERO1*(1.601-ALOG(B))
  203        1+2.*E2PRIM*ALOG(B)-3.42*E2PRIM+ALPHA*BETA+2.*E1PRIM*EZERO1*(2.*B*3
  204        2+2.*B-1.)/B**3+44*E2PRIM/3./B
  205         WRITE (6,16) B, GUESSL
  206         DO 17  NMB = 1, NUMBER
  207         DO 18 ITRATE=1,50
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      12345678901234567890123456789012345678901234567890123456789012345678901234567890
CARD
  208       OGAMMA1(NMB)=EQUCON(NMB)/(EZERO1-ONSAG1*ROOTCN(NMB)*SQRT(GAMMA2(NMB
  209      1))+E*CONCEN(NMB)*GAMMA2(NMB)*ALOG10(6.*E1PRIM*CONCEN(NMB)*GAMMA2(N
  210      2MB))+GUESSL*CONCEN(NMB)*GAMMA2(NMB))
  211         ITRGAM = ITRATE + 1
  212         IF (ABS(GAMMA1(NMB)-GAMMA2(NMB)).LT..00005) GO TO 19
  213         GAMMA2(NMB)=GAMMA1(NMB)
  214      18 CONTINUE
  215         WRITE (6,20) NMB , GAMMA1(NMB)
  216         KICKER = 1
  217         GO TO 21
  218      19 WRITE (6,22) NMB, GAMMA1(NMB), ITRGAM
  219         GAMMA2(NMB)=GAMMA1(NMB)
  220      21 CONTINUE
  221      17 CONTINUE
  222         S=ONSAG1
  223         CONST(1)=EZERO1
  224         CONST(3)=GUESSL
  225         CONST(2)=3000.                                                CHECK 3
  226         IF (KICKER.NE.1) GO TO 23
  227         WRITE (6,24)
  228         CALL EXIT
  229      23 CONTINUE
  230         DO 34 I=1,NUMBER
  231         X(I)=CONCEN(I)*GAMMA2(I)
  232         Y(I)=EQUCON(I)
  233         SIGX(I)=X(I)*.002
  234         SIGY(I)=Y(I)*.002
  235      34 CONTINUE
  236         CALL SQUARE(NROW,NUMBER,X,EQUCON,CONST,S,E,E1PRIM,SIGX,SIGY,YCALX,
  237        1SIG,SUM,DEV,SIGSQ,VAR,SIGEXT,NCOL,F,ALPHA)
  238         EZERO1 = CONST(1)
  239         ONSAG1 = ALPHA * EZERO1 + BETA
  240         EXPB=CONST(2)/2.5227E+21*(DIELCT*TKELVN/16.7099E-4)**3
  241      39 CONTINUE
  242         CALB=ALOG(EXPB)+3.*ALOG(B)
  243         IF(B.GT.25.) GO TO 40
  244         IF(B.LT.3.05)  GO TO 40
  245         IF(ABS(CALB-B).LT..001) GO TO 40
  246         B=CALB
  247         GO TO 39
  248      40 CONTINUE
  249         CALCUL=2.*E1PRIM*EZERO1*(1.601-ALOG(B))
  250        1+2.*E2PRIM*ALOG(B)-3.42*E2PRIM+ALPHA*BETA+2.*E1PRIM*EZERO1*(2.*B*B
  251        2+2.*B-1.)/B**3+44*E2PRIM/3./B
  252         A=16.7099E-4/DIELCT/TKELVN/B
  253         WRITE(6,F1000)
  254         WRITE(6,101)
  255         DO 38 I=1,NUMBER
  256         WRITE(6,102)CONCEN(I),GAMMA2(I),X(I),Y(I),YCALX(I),F(4,I)
  257      38 CONTINUE
  258         WRITE(6,103)
  259         WRITE(6,104)(CONST(I),I=1,NROW),SUM
  260         WRITE(6,105)(SIG(I),I=1,NROW),SIGSQ
  261         WRITE(6,108)
  262         WRITE(6,104)B,A,CALCUL
  263         WRITE(6,205)SIGEXT
  264         CONST(3)=(CONST(3)+GUESSL)/2.
  265         GUESSL=CONST(3)
  266         LAP = 0
  267         DO 36 NMB=1,NUMBER
  268         DO 500  ITER=1,50
  269         GAMMA3(NMB)=EQUCON(NMB)/(EZERO1-ONSAG1*ROOTCN(NMB)*SQRT(GAMMA2(NMB
  270        1))+E*CONCEN(NMB)*GAMMA2(NMB)*ALOG10(6.*E1PRIM*CONCEN(NMB)*GAMMA2(N
  271        2MB))+GUESSL*CONCEN(NMB)*GAMMA2(NMB))
  272         IF(ABS(GAMMA3(NMB)-GAMMA2(NMB)).LT.0.00005) GO TO 500
  273         GAMMA2(NMB)=GAMMA3(NMB)
  274     500 CONTINUE
  275         ITRGAM=1
  276         IF(ABS(GAMMA1(NMB)-GAMMA2(NMB)).LT..0005)  ITRGAM=0
  277         IF(ITRGAM.NE.0) LAP=1
  278         GAMMA1(NMB)=GAMMA2(NMB)
  279         WRITE (6,22) NMB, GAMMA1(NMB), ITRGAM
  280      36 CONTINUE
  281         IF(LAP.EQ.0) GO TO 37
  282         E = 2.30259* (E1PRIM * EZERO1 - E2PRIM)
  283         S=ALPHA*EZERO1+BETA
  284         GO TO 23
  285      37 CONTINUE
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      12345678901234567890123456789012345678901234567890123456789012345678901234567890
CARD
 286        JONES=JONES+1
 287        IF(JONES.EQ.1) GO TO 23
 288        VMAX=VAR(1)
 289        DO 89 I=1,NUMBER
 290        TEST=VMAX-VAR(I)
 291        IF (TEST.GT.0.) GO TO 89
 292        VMAX=VAR(I)
 293        JAM=I
 294     89 CONTINUE
 295        DEV=VAR(JAM)/SIGEXT
 296        PRINT 206,DEV
 297        IF(DEV.LT.2.) GO TO 71
 298        WRITE(6,201)X(JAM),Y(JAM),DEV
 299        WRITE(6,202)(CONST(I),I=1,NROW)
 300        WRITE(6,203)(SIG(I),I=1,NROW)
 301        WRITE(6,204)SIGEXT
 302        NUMBER=NUMBER-1
 303        DO 110 I=JAM,NUMBER
 304        CONCEN(I)=CONCEN(I+1)
 305        EQUCON(I)=EQUCON(I+1)
 306        GAMMA2(I)=GAMMA2(I+1)
 307        ROOTCN(I)=ROOTCN(I+1)
 308    110 CONTINUE
 309        GO TO 23
 310     71 CONTINUE
 311        WRITE(6,F1000)
 312     41 FORMAT(8X,'B',10X,'L'/)
 313     43 FORMAT (5X,F5.0,1PE15.4)
 314        WRITE (6,41)
 315        DO 42 I=1,25
 316        B=I
 317        CALCUL=2.*E1PRIM*EZERO1*(1.601-ALOG(B))
 318       1+2.*E2PRIM*ALOG(B)-3.42*E2PRIM+ALPHA*BETA+2.*E1PRIM*EZERO1*(2.*B*B
 319       2+2.*B-1.)/B**3+44*E2PRIM/3./B
 320        WRITE(6,43)B,CALCUL
 321     42 CONTINUE
 322     47 CONTINUE
 323        WRITE (6,7)
 324        STOP
 325        END
 326  C*****************************************************************************
 327  C**************************  SUBROUTINE SUBPROGRAM  **************************
 328  C*****************************************************************************
 329  C*****************************  SUBPROGRAM TITLE  ****************************
 330  C                                   SQUARE
 331  C*****************************************************************************
 332  C**************************  VARIABLES TRANSFERRED  **************************
 333        SUBROUTINE SQUARE(NROW,NN,X,Y,CONST,S,E,E1PRIM,SIGX,SIGY,YCALX,SIG
 334       1,SUM,DEV,SIGSQ,VAR,SIGEXT,NCOL,F,ALPHA)
 335  C*****************************************************************************
 336  C************************  DOUBLE PRECISION STATEMENT  ************************
 337        DOUBLE PRECISION G,H,PIVOT1,PIVOT2,DSQRT
 338  C*****************************************************************************
 339  C**************************  DIMENSION STATEMENT  ****************************
 340        DIMENSION Y(20),X(20),CONST(3),SIGY(20),SIGX(20),YCALX(20),SIG(3),
 341       1VAR(20),F(7,20),FX(20),FY(20),FXY(20),G(3,4),H(3,4),SX(20),ETERM(2
 342       10),XLTERM(20),XYKTRM(20),TAUSQ(20),TAU(20)
 343  C*****************************************************************************
 344  C**************************  FORMAT STATEMENTS  ******************************
 345      4 FORMAT (6X,4E20.7)
 346      6 FORMAT(1H1)
 347      7 FORMAT(//6X,'LAMBDA ZERO',10X,'S TERM',10X,'E TERM',10X,'L TERM',
 348       110X,'K TERM',6X,'CAL LAMBDA',11X,'SIG X',11X,'SIG Y'/)
 349      9 FORMAT (//19H       NORMAL MATRIX//)
 350     12 FORMAT (//20H       INVERSE MATRIX//)
 351     13 FORMAT(1X,8E16.7)
 352     16 FORMAT(///8X,'F1',14X,'F2',14X,'F3',14X,'F0',12X,'F0*F0/L',11X,'FX    16-1
 353       1',14X,'FY',15X,'L'/)
 354  C*****************************************************************************
 355  C*****************************  SUBPROGRAM  **********************************
 356        NZRO=NROW+2
 357        SUM=0.
 358     15 CONTINUE
 359        SUMP=SUM
 360        SUM=0.0
 361        POINTS=NN
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      12345678901234567890123456789012345678901234567890123456789012345678901234567890
CARD
  362         DO 20 I=1, NN
  363         TAUSQ(I) = 6.*E1PRIM*X(I)
  364         TAU(I) = SQRT(TAUSQ(I))
  365         F(1,I)=1.0 -ALPHA*SQRT(X(I)) +E1PRIM*X(I)*ALOG(TAUSQ(I))
  366         F(2,I)=-X(I)*Y(I)*EXP(-2.*TAU(I))
  367         F(3,I)=X(I)
  368        OF(4,I)=CONST(1)-Y(I)-S*SQRT(X(I))+E*X(I)*ALOG10(TAUSQ(I)) +
  369        1CONST(3)*X(I)+CONST(2)*F(2,I)
  370         FX(I)=-.5*S/SQRT(X(I))+E*ALOG10(TAUSQ(I))+E/2.30259+CONST(3)
  371        1+CONST(2)*F(2,I)/X(I)+CONST(2)*TAU(I)*Y(I)*EXP(-2.*TAU(I))
  372         FY(I)=CONST(2)*F(2,I)/Y(I)-1.
  373         FXY(I)=(FX(I)*SIGX(I))**2+(FY(I)*SIGY(I))**2
  374         F(NZRO,I)=F(NCOL,I)*F(NCOL,I)/FXY(I)
  375         SUM=SUM+F(NZRO,I)
  376         VAR(I)=SQRT(F(NCOL+1,I))
  377         YCALX(I)=Y(I)+F(NCOL,I)
  378         SX(I)=-S*SQRT(X(I))
  379         ETERM(I)=E*X(I)*ALOG10(TAUSQ(I))
  380         XYKTRM(I)=CONST(2)*F(2,I)
  381         XLTERM(I)=CONST(3)*X(I)
  382      20 CONTINUE
  383         DO 32 K=1,NROW
  384         DO 31 L=1,NCOL
  385         G(K,L)=0.0
  386         DO 30 I=1,NN
  387         G(K,L)=G(K,L)+F(K,I)*F(L,I)/FXY(I)
  388         H(K,L)=G(K,L)
  389      30 CONTINUE
  390      31 CONTINUE
  391      32 CONTINUE
  392         DO 45 I=1,NROW
  393         PIVOT1 = 1.0/H(I,I)
  394         H(I,I) = PIVOT1
  395         DO 40 J=1,NCOL
  396         IF(J.EQ.I) GO TO 40
  397         H(I,J) = PIVOT1*H(I,J)
  398      40 CONTINUE
  399         DO 43 K=1,NROW
  400         IF(K.EQ.I) GO TO 43
  401         PIVOT2 = H(K,I)
  402         H(K,I) = -PIVOT2*PIVOT1
  403         DO 41 L=1,NCOL
  404         IF(L.EQ.I) GO TO 41
  405         H(K,L) = H(K,L)-PIVOT2*H(I,L)
  406      41 CONTINUE
  407      43 CONTINUE
  408      45 CONTINUE
  409         CON=NROW
  410         SIGSQ=SUM/(POINTS-CON)
  411         SIGEXT= SQRT(SIGSQ)
  412         DO 33 I=1,NROW
  413         CONST(I)=CONST(I)-H(I,NCOL)
  414         SIG(I)=DSQRT(H(I,I))*SIGEXT
  415      33 CONTINUE
  416         IF (ABS((SUMP-SUM)*1.E3).GE.SUM)GO TO 15
  417         WRITE(6,6)
  418         WRITE (6,16)
  419         DO 78 I=1,NN
  420         WRITE(6,13)(F(L,I),L=1,NZRO),FX(I),FY(I),FXY(I)
  421      78 CONTINUE
  422         WRITE (6,9)
  423         DO 79 K=1,NROW
  424         WRITE(6,4)(G(K,L),L=1,NCOL)
  425      79 CONTINUE
  426         WRITE (6,12)
  427         DO 80 K=1,NROW
  428         WRITE(6,4)(H(K,L),L=1,NCOL)
  429      80 CONTINUE
  430         WRITE(6,7)
  431         WRITE(6,13)(CONST(I),SX(I),ETERM(I),XLTERM(I),XYKTRM(I),YCALX(I),
  432        1SIGX(I),SIGY(I),I=1,NN)
  433         RETURN
  434         END
  435   C*******************************************************************************
  436   C*********************************  DATA CARDS  ********************************
  437   C*******************************************************************************
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VITA

Charles William Jones

Candidate for the Degree of

Doctor of Philosophy

Thesis: ELECTROLYTIC CONDUCTANCE OF LITHIUM BROMIDE IN ACETONE AND ACETONE-BROMOSUCCINIC ACID SOLUTION

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